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[Document Name] Petition for Patent [Docket No.] NPX1030009 [Filing Date] March 27, 2003 [Address] Commissioner, Patent Office [International Patent H01M 4/02 H01M 4/04 Classification [Inventor] Address c/o SANYO ELECTRIC CO., LTD. 2-5-5, Keihanhondori, Moriguchishi, Osaka 570-8677, JAPAN [Name] Masaharu ITAYA [Inventor] [Address] c/o SANYO ELECTRIC CO., LTD. 2-5-5, Keihanhondori, Moriguchishi, Osaka 570-8677, JAPAN [Name] Masahide MIYAKE [Inventor] [Address] c/o SANYO ELECTRIC CO., LTD. 2-5-5, Keihanhondori, Moriguchishi, Osaka 570-8677, JAPAN [Name] Masahisa FUJIMOTO [Applicant] [Identification No.] 000001889 [Name] SANYO ELECTRIC CO., LTD. [Attorney] [Identification No.] 100098305 [Patent Attorney] [Name] Yoshito FUKUSHIMA [Telephone No.] 06-6330-5625 [Payment of Fees] [Prepayment Book No.] 032920 [Amount to be paid] ¥21,000

Attached Documents

[Item]	Specification	1
[Item]	Drawings	1
[Item]	Abstract	1
[Identification No.	0006012	
of General Power		
[Requirement of Proof]	Yes	-

[Document Name] Specification

[Title of the Invention] Non-aqueous electrolyte secondary battery

[Scope of Claim for Patent]

5 [Claim 1] A non-aqueous electrolyte secondary battery characterized by comprising a positive electrode, a negative electrode, and a non-aqueous electrolyte, wherein

said positive electrode includes elemental sulfur, and said negative electrode includes silicon that stores lithium.

10 [Claim 2] The non-aqueous electrolyte secondary battery as recited in Claim 1, characterized in that said non-aqueous electrolyte includes a room temperature molten salt having a melting point of not higher

than 60°C.

15 [Claim 3] The non-aqueous electrolyte secondary battery as recited in Claim 1 or 2, characterized in that said non-aqueous electrolyte includes a quaternary ammonium salt.

[Claim 4] The non-aqueous electrolyte secondary

20 battery as recited in Claim 2 or 3, characterized in that
 said non-aqueous electrolyte further includes at least
 one type of solvent selected from the group consisting of
 cyclic ether, chain ether, and fluorinated carbonate.

[Claim 5] A non-aqueous electrolyte secondary battery

characterized by comprising a positive electrode, a negative electrode, and a non-aqueous electrolyte, wherein

said negative electrode includes silicon that stores lithium, and

said non-aqueous electrolyte includes a room temperature molten salt having a melting point of not higher than 60°C and a reduction product of elemental sulfur.

[Claim 6] The non-aqueous electrolyte secondary battery as recited in Claim 5, characterized in that said positive electrode includes elemental sulfur.

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[Claim 7] The non-aqueous electrolyte secondary battery as recited in Claim 5 or 6, characterized in that said reduction product of elemental sulfur is obtained by reducing elemental sulfur in a room temperature molten salt having a melting point of not higher than 60°C and an organic electrolyte.

[Claim 8] The non-aqueous electrolyte secondary battery as recited in any of Claims 1 to 7, characterized in that

20 said silicon is an amorphous silicon thin film or a microcrystalline silicon thin film.

[Claim 9] The non-aqueous electrolyte secondary battery as recited in Claim 2 or any of Claims 5 to 7, characterized in that

said room temperature molten salt includes at least one type selected from the group consisting of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide, trimethyloctylammonium 5 bis(trifluoromethylsulfonyl)imide, trimethylallylammonium bis(trifluoromethylsulfonyl)imide, trimethylhexylammonium bis(trifluoromethylsulfonyl)imide, trimethylethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, trimethylallylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, 10 trimethylpropylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, tetraethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, 15 triethylmethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, 1-ethyl-3-methylimidazolium bis (pentafluoroethylsulfonyl) imide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 20 1-ethyl-3-methylimidazolium tetrafluoroborate, and

[Claim 10] The non-aqueous electrolyte secondary battery as recited in Claim 3, characterized in that

1-ethyl-3-methylimidazolium pentafluoroborate.

said quaternary ammonium salt includes at least one type selected from the group consisting of trimethylpropylammonium

bis(trifluoromethylsulfonyl)imide, trimethyloctylammonium bis(trifluoromethylsulfonyl)imide, trimethylallylammonium bis(trifluoromethylsulfonyl)imide, trimethylhexylammonium bis(trifluoromethylsulfonyl)imide, trimethylethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, trimethylallylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, trimethylpropylammonium

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- 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, tetraethylammonium
- 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, triethylmethylammonium
- 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, tetramethylammonium tetrafluoroborate, tetramethylammonium hexafluorophosphate, tetraethylammonium tetrafluoroborate, and tetraethylammonium hexafluorophosphate.
- 20 [Claim 11] The non-aqueous electrolyte secondary battery as recited in Claim 4, characterized in that

said cyclic ether include at least one type selected from the group consisting of 1,3-dioxolane,
4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl

25 tetrahydrofuran, propylene oxide, 1,2-butylene oxide,

1,4-dioxiane, 1,3,5-trioxane, furan, 2-methy furan,
1,8-cineole, and crown ether; said chain ether includes at
lest one type selected from the group consisting of

diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl ether, butyl phenyl ether, pentyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane,

1,2-dimethoxyethane, diethyl ether, dipropyl ether,

10 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether; and said fluorinated carbonate includes at least one type selected from the group consisting of trifluoropropylene carbonate and fluoroethyl carbonate.

[Claim 12] The non-aqueous electrolyte secondary battery as recited in any of Claims 1 to 11, characterized in that

20 a conductive agent is added to said positive electrode.

[Claim 13] The non-aqueous electrolyte secondary battery as recited in any of Claims 1 to 12, characterized in that

said non-aqueous electrolyte includes γ -butyrolactone. 25 [Detailed Description of the Invention]

[0001]

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[Technical Field to which the Invention Belongs]

The present invention relates to a non-aqueous
electrolyte secondary battery composed of a positive
electrode, a negative electrode and non-aqueous electrolyte.
[0002]

[Conventional Art]

In recent years, as one of the secondary batteries having high power and high energy density, non-aqueous electrolyte secondary batteries with high electromotive forces have been made available in which the oxidation and reduction of lithium using non-aqueous electrolytes is utilized.

[0003]

15 The currently practical lithium secondary batteries have lithium cobaltate (LiCoO₂) or lithium manganate (LiMn₂O₄) as positive electrode materials, and carbon materials as negative electrode materials. In addition, these batteries have non-aqueous electrolytes including electrolyte salts of lithium salts, such as LiBF₄ and LiPF₆, dissolved in organic solvents of ethylene carbonate, diethyl carbonate, or the like.

[0004]

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However, portable equipment requires secondary batteries having longer duration, and hence further increased

capacity and energy density of lithium secondary batteries are required.

[0005]

As a negative electrode material capable of storage and release of lithium while exhibiting high capacity, the use of a silicon thin film formed by being deposited on a negative electrode current collector has been proposed (refer to Patent Documents 1 and 2.) This negative electrode material allows a negative electrode capacity of at least 3000 to 4000 mAh/g.

[0006]

[Patent Document 1]

JP-2001-266851-A

[Patent Document 2]

15 JP-2002-83594-A

[Patent Document 3]

JP-4-267073-A

[Patent Document 4]

JP-8-115724-A

20 [0007]

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[Problems to be Solved by the Invention]

However, for the preparation of a lithium secondary battery having the silicon material as a negative electrode and lithium cobaltate as a positive electrode, it is required to considerably increase the thickness of the positive

electrode active material layer in order to balance the positive and negative electrode capacities. This may make it difficult for the electrolyte to penetrate into the positive electrode active material layer during a

5 manufacturing process, and may further cause a shortage of the electrolyte in the positive electrode active material layer during charge-discharge cycles, resulting in deterioration of the charge-discharge cycle characteristics. For this reason, there exits a need for the development of positive electrode materials having a high electrode capacity balanced with the high negative electrode capacity.

In recent years, the use of an organic disulfide compound, such as DMcT (2,5-dimercapto-1,3,4-thiadiazole), as a positive electrode material for achieving high capacity and high energy density has been proposed. However, the organic disulfide compound used as a positive electrode material react reversibly with lithium only at elevated temperatures of 60°C or higher. Therefore, the use of organic disulfide compound in general non-aqueous electrolyte secondary batteries has been difficult.

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Moreover, in recent years, a secondary battery has been proposed capable of the charge-discharge reaction at room temperature using a positive electrode material obtained from

the above-mentioned organic disulfide compound, such as DMcT, mixed with a conductive polymer, such as polyaniline (refer to Patent Documents 3 and 4.)
[0010]

In the case of the above-mentioned positive electrode active material using the organic disulfide compound, however, the disulfide bonds are involved with the charge-discharge reaction, and other parts including carbon atoms and hydrogen atoms do not contribute to the reaction.

Therefore, it has been difficult to further increase a capacity per weight.

[0011]

An object of the present invention is to provide a non-aqueous electrolyte secondary battery having increased capacity and energy density.

[0012]

[0013]

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[Means for Solving the Problems and Effects of the Invention]

A non-aqueous electrolyte secondary battery according to a first invention comprises a positive electrode, a negative electrode, and a non-aqueous electrolyte, the positive electrode including elemental sulfur, the negative electrode including silicon that stores lithium.

In the non-aqueous electrolyte secondary battery according to the present invention, the combination of the

positive electrode including elemental sulfur and the negative electrode including silicon that stores lithium enables the elemental sulfur in the positive electrode and the silicon in the negative electrode to react reversibly with lithium at relatively low temperatures. In this case, the use of silicon that stores lithium can result in increased negative electrode capacity. Moreover, the use of elemental sulfur in the positive electrode enables increased capacity per unit weight, compared with that obtained using an organic disulfide compound. Accordingly, the negative electrode capacity and positive electrode capacity can be easily balanced, so that increased capacity and energy density can be realized.

[0014]

The non-aqueous electrolyte may include a room temperature molten salt having a melting point of not higher than 60°C. In this case, the reversible reaction of the silicon in the negative electrode and the elemental sulfur in the positive electrode with lithium can be easily carried out also at room temperature, so as to facilitate the charging/discharging reaction at room temperature. Room temperature molten salts having melting points of not higher than 60°C are liquids containing only ions, having fire-resistance and no vapor pressure, and therefore, they are not decomposed or burned even at the time of abnormal

operations, such as overcharging, and can be safely used without the provision of a protection circuit or the like. [0015]

The non-aqueous electrolyte may include a quaternary ammonium salt. In this case, the reversible reaction of the silicon in the negative electrode and the elemental sulfur in the positive electrode with lithium can be easily carried out also at room temperature, so as to facilitate the charging/discharging reaction at room temperature.

10 [0016]

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The non-aqueous electrolyte may further include at least one type of solvent selected from the group consisting of cyclic ether, chain ether, and fluorinated carbonate. In this case, the reversible reaction of the silicon in the negative electrode and the elemental sulfur in the positive electrode with lithium can be more easily carried out also at room temperature, so as to further facilitate the charging/discharging reaction at room temperature.

A non-aqueous electrolyte secondary battery according to a second invention comprises a positive electrode, a negative electrode, and a non-aqueous electrolyte, the negative electrode including silicon that stores lithium, the non-aqueous electrolyte including a room temperature molten

salt having a melting point of not higher than 60°C and a reduction product of elemental sulfur.

In the non-aqueous electrolyte secondary battery according to the present invention, the inclusion of the room temperature molten salt having a melting point of not higher than 60°C and the reduction product of elemental sulfur in the non-aqueous electrolyte enables the silicon in the negative electrode to easily react with lithium also at room temperature, so as to facilitate the charging/discharging at room temperature. Accordingly, increased capacity and energy density can be realized.

[0019]

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The positive electrode may include elemental sulfur. In this case, the combination of the positive electrode including elemental sulfur and the negative electrode including silicon that stores lithium enables the elemental sulfur in the positive electrode and the silicon in the negative electrode to reversibly react with lithium. In this case, the use of silicon that stores lithium for the negative electrode can increase the negative electrode capacity, and the use of elemental sulfur for the positive electrode can increase the positive electrode capacity. Accordingly, the negative electrode capacity and the positive electrode

capacity can be easily balanced, so that further increased capacity and energy density can be realized.
[0020]

The reduction product of elemental sulfur may be

5 obtained by reducing elemental sulfur in a room temperature
molten salt having a melting point of not higher than 60°C
and an organic electrolyte. In this case, the reversible
reaction of the silicon in the negative electrode and the
elemental sulfur in the positive electrode with lithium can

10 be more easily carried out also at room temperature, so as
to further facilitate the charging/discharging reaction at
room temperature.

The silicon may be an amorphous silicon thin film or a microcrystalline silicon thin film. In this case, further increased negative electrode capacity can be achieved.

[0021]

[0022]

The room temperature molten salt may include at least one type selected from the group consisting of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2), \ trimethyloctylammonium \\ bis(trifluoromethylsulfonyl)imide$

 $\label{eq:charge} \mbox{((CH$_3)$}_3\mbox{N}^+\mbox{(C$_8$}\mbox{H$_{17}$)}\mbox{N}^-\mbox{(SO$_2$CF$_3$)$}_2\mbox{), trimethylallylammonium} \\ \mbox{bis(trifluoromethylsulfonyl)imide}$

25 $((CH_3)_3N^+(Allyl)N^-(SO_2CF_3)_2$, trimethylhexylammonium

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bis(trifluoromethylsulfonyl)imide
    ((CH_3)_3N^+(C_6H_{13})N^-(SO_2CF_3)_2), trimethylethylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((CH_3)_3N^+(C_2H_5)(CF_3CO)N^-(SO_2CF_3)), trimethylallylammonium
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    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((CH_3)_3N^+(Allyl)(CF_3CO)N^-(SO_2CF_3)), trimethylpropylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((CH_3)_3N^+(C_3H_7)(CF_3CO)N^-(SO_2CF_3)), tetraethylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((C_2H_5)_4N^+(CF_3CO)N^-(SO_2CF_3)), triethylmethylammonium
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    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((C_2H_5)_3N^+(CH_3)(CF_3CO)N^-(SO_2CF_3)),
    1-ethyl-3-methylimidazolium
    bis (pentafluoroethylsulfonyl) imide
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2C_2F_5)_2),
15
    1-ethyl-3-methylimidazolium
    bis(trifluoromethylsulfonyl)imide
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2CF_3)_2),
    1-ethyl-3-methylimidazolium tetrafluoroborate
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)BF_4^-), and 1-ethyl-3-methylimidazolium
20
    pentafluoroborate ((C_2H_5)(C_3H_3N_2)^+(CH_3)PF_6^-).
    [0023]
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type selected from the group consisting of
trimethylpropylammonium

The quaternary ammonium salt may include at least one

bis(trifluoromethylsulfonyl)imide, trimethyloctylammonium bis(trifluoromethylsulfonyl)imide, trimethylallylammonium bis(trifluoromethylsulfonyl)imide, trimethylhexylammonium bis(trifluoromethylsulfonyl)imide, trimethylethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, trimethylallylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, trimethylpropylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, tetraethylammonium

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2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide, triethylmethylammonium

2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide,
tetramethylammonium tetrafluoroborate, tetramethylammonium
hexafluorophosphate, tetraethylammonium tetrafluoroborate,
and tetraethylammonium hexafluorophosphate.
[0024]

The cyclic ether may include at least one type selected from the group consisting of 1,3-dioxolane,

4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran, propylene oxide, 1,2-butylene oxide, 1,4-dioxiane, 1,3,5-trioxane, furan, 2-methy furan, 1,8-cineole, and crown ether; the chain ether may include at lest one type selected from the group consisting of

25 1,2-dimethoxyethane, diethyl ether, dipropyl ether,

diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl ether, butyl phenyl ether, pentyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether; and the fluorinated carbonate may include at least one type selected from the group consisting of trifluoropropylene carbonate and fluoroethyl carbonate.

A conductive agent may be added to the positive electrode. This enhances the conductivity of the positive electrode. As a result, the charge-discharge characteristics can be enhanced.

Further, the non-aqueous electrode may include

20 γ-butyrolactone. In this case also, the reversible reaction of the silicon in the negative electrode and the elemental sulfur in the positive electrode with lithium can be easily carried out at room temperature, so as to facilitate the charging/discharging reaction at room temperature.

25 [0027]

[0026]

[Embodiments of the Invention]

Description will, hereinafter, be made of a non-aqueous electrolyte secondary battery according to one embodiment of the present invention.

5 [0028]

The non-aqueous electrolyte secondary battery according to the present embodiment comprises a negative electrode, a positive electrode, and a non-aqueous electrolyte.

10 [0029]

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[0030]

The positive electrode has a positive electrode active material made of a mixture of elemental sulfur, a conductive agent, and a binder. As the conductive agent, a conductive carbon material, for example, may be used. It is noted that addition of too small an amount of conductive carbon material cannot sufficiently enhance the conductivity in the positive electrode, whereas addition of an excessive amount of the material decreases the ratio of elemental sulfur in the positive electrode, and fails to achieve high capacity. Accordingly, the amount of carbon material may be set in the range of 5 to 84% by weight of the whole positive electrode active material, preferably, in the range of 5 to 54% by weight, more preferably, in the range of 5 to 20% by weight.

As the negative electrode, silicon that stores lithium is used. For example, an amorphous silicon thin film or a microcrystalline silicon film is formed on a current collector made of a copper foil having an electrolytically treated surface. A thin film made of a mixture of amorphous silicon and microcrystalline silicon may also be used. As a film formation method, sputtering, plasma CVD (chemical vapor deposition), or the like may be used. In particular, it is preferable to use silicon with large capacity, as proposed in JP-2001-266851-A and JP-2002-83594-A. This enables a non-aqueous electrolyte secondary battery having increased energy density. In place of the silicon thin film, silicon powder formed using a binder may also be used.

[0032]

As the non-aqueous electrolyte, a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C and a lithium salt may be used. Room temperature molten salts are liquids containing only ions, having fire-resistance and no vapor pressure. Hence, they are not decomposed or burned even at the time of abnormal operations, such as overcharging, and can be safely used without the provision of a protection circuit or the like.

It is necessary for the room temperature molten salt to remain liquid in a broad room temperature range, in general, in the range of -20°C to 60°C . It is desired that the room temperature molten salt have a conductivity of not less than 10^{-4}S/cm .

[0033]

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By the addition of a lithium salt, a room temperature molten salt will probably have a lower melting point than the melting point of each of the two types of salts alone, and these are maintained in a liquid state.

[0034]

As the non-aqueous electrolyte salt, a non-aqueous electrolyte salt including a quaternary ammonium salt and a lithium salt may also be used.

15 [0035]

Further, as the non-aqueous electrolyte salt, a non-aqueous electrolyte salt including a room temperature molten salt having a melting point of not higher than 60°C and a reduction product of elemental sulfur may be used. The reduction product of elemental sulfur may be obtained by reducing elemental sulfur in a room temperature molten salt having a melting point of not higher than 60°C and an organic electrolyte.

[0036]

As the non-aqueous electrolyte, γ -butyrolactone may also be used.

As the room temperature molten salt, a quaternary ammonium salt or an imidazolium salt may be used, for example. Specifically, as the room temperature molten salt, at least one type selected from trimethylpropylammonium

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$, trimethyloctylammonium bis(trifluoromethylsulfonyl)imide

bis(trifluoromethylsulfonyl)imide

 $\begin{array}{ll} & \text{((CH_3)_3N^+(C_8H_{17})N^-(SO_2CF_3)_2), trimethylallylammonium} \\ & \text{bis(trifluoromethylsulfonyl)imide} \\ & \text{((CH_3)_3N^+(Allyl)N^-(SO_2CF_3)_2, trimethylhexylammonium} \\ & \text{bis(trifluoromethylsulfonyl)imide} \\ \end{array}$

((CH3)3N+(C6H13)N-(SO2CF3)2), trimethylethylammonium

15 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide $((CH_3)_3N^+(C_2H_5)(CF_3CO)N^-(SO_2CF_3)), \ trimethylallylammonium \\ 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide \\ ((CH_3)_3N^+(Allyl)(CF_3CO)N^-(SO_2CF_3)), \ trimethylpropylammonium \\ 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide$

20 $((CH_3)_3N^+(C_3H_7)(CF_3CO)N^-(SO_2CF_3))$, tetraethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide $((C_2H_5)_4N^+(CF_3CO)N^-(SO_2CF_3))$, triethylmethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide $((C_2H_5)_3N^+(CH_3)(CF_3CO)N^-(SO_2CF_3))$,

25 1-ethyl-3-methylimidazolium

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bis (pentafluoroethylsulfonyl) imide  ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2C_2F_5)_2),   1-ethyl-3-methylimidazolium  bis (trifluoromethylsulfonyl) imide  ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2CF_3)_2),   1-ethyl-3-methylimidazolium tetrafluoroborate \\  ((C_2H_5)(C_3H_3N_2)^+(CH_3)BF_4^-), 1-ethyl-3-methylimidazolium \\  pentafluoroborate ((C_2H_5)(C_3H_3N_2)^+(CH_3)PF_6^-), and the like. \\  [0037]
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As the quaternary ammonium salt, instead of the above-mentioned quaternary ammonium salt for use as a room temperature molten salt, at least one type selected from tetramethylammonium tetrafluroborate ((CH₃) $_4$ N $^+$ BF $_4$ $^-$), tetramethylammonium hexafluorophosphate ((CH₃) $_4$ N $^+$ PF $_6$ $^-$), tetraethylammonium tetrafluroborate ((C $_2$ H $_5$) $_4$ N $^+$ BF $_4$ $^-$), tetraethylammonium hexafluorophosphate ((C $_2$ H $_5$) $_4$ N $^+$ PF $_6$ $^-$), and the like may be use. [0038]

It is noted that the above-mentioned non-aqueous

20 electrolyte may include an organic solvent, such as ethylene
carbonate, diethyl carbonate, dimethyl carbonate, propylene
carbonate, cyclic ether, chain ether, fluorinated carbonate,
in addition to the room temperature molten salt or quaternary
ammonium salt.

25 [0039]

As the cyclic ether, at least one type selected from 1,3-dioxolane, 4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl tetrahydrofuran, propylene oxide, 1,2-butylene oxide, 1,4-dioxiane, 1,3,5-trioxane, furan, 2-methy furan, 1,8-cineole, crown ether, and the like may be used. [0040]

As the chain ether, at least one type selected from 1,2-dimethoxyethane, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl 10 ether, butyl phenyl ether, pentyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl 15 ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether, and the like may be used. As the fluorinated carbonate, at least one type selected from trifluoropropylene carbonate, fluoroethyl carbonate, and the like may be used. 20 [0041]

As the lithium salt to be added to the non-aqueous electrolyte, a lithium salt used as an electrolyte in general non-aqueous electrolyte secondary battery may be used. For example, at least one type selected from LiBF4, LiPF6, LiCF3

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 SO_3 , LiC_4 F_9 SO_3 , $LiN(CF_3$ SO_2)₂, $LiN(C_2$ F_5 SO_2)₂, $LiN(CF_3$ SO_2)(COCF₃), and LiAsF₆ may be used. [0042]

Another possibility is the gelation of the non-aqueous 5 electrolyte using polyethylene oxide (PEO), for example, for preventing the elution of elemental sulfur to allow the reversible reaction of the elemental sulfur. As the non-aqueous electrolyte, a gelled polymer electrolyte in which a polymer electrolyte such as polyethylene oxide, polyacrylonitrile, or the like is impregnated with an 10 electrolyte salt, or an inorganic solid electrolyte such as LiI or Li₃N may also be used.

[0043]

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In the non-aqueous electrolyte secondary battery according to the present embodiment, the combination of the positive electrode including elemental sulfur and the negative electrode including silicon that stores lithium allows the elemental sulfur in the positive electrode and the silicon in the negative electrode to react reversibly with the lithium at relatively low temperatures. In this case, high negative electrode capacity can be obtained using silicon that stores lithium. Moreover, the use of elemental sulfur in the positive electrode allows increased capacity per unit weight compared with that obtained using an organic disulfide compound. Consequently, the negative and positive

electrode capacities can be easily balanced, and increased capacity and energy density can be realized. [0044]

In the case of the non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C, a quaternary ammonium salt, a reduction product of elemental sulfur, or γ -butyrolactone, the silicon in the negative electrode and elemental sulfur in the positive electrode easily react reversibly with lithium also at room temperature, and hence the charge-discharge reaction at room temperature can be facilitated.

(Examples)

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[0045]

It will now be apparent from the citation of Examples

that the non-aqueous electrolyte secondary battery according
to the present invention in which elemental sulfur is used
for the positive electrode and a silicon material is used for
the negative electrode can be appropriately
charged/discharged at room temperature, and has much

increased energy density. It will be recognized that the
following examples merely illustrate the practice of the
non-aqueous electrolyte secondary battery in the present
invention but are not intended to be limiting thereof.
Suitable changes and modifications can be effected without
departing the scope of the present invention.

[0046]

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In Inventive Examples 1 to 20 and Comparative Examples 1 to 5 described below, the test cell shown in Fig. 1 was prepared to evaluate a positive electrode including sulfur and a negative electrode including a silicon material.

[0047]

As shown in Fig. 1, a non-aqueous electrolyte 14 was poured into a test cell vessel 10, and a working electrode 11 and a reference electrode 13 were immersed in the non-aqueous electrolyte 14.

[0048]

In Inventive Examples 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, and Inventive Examples 1 to 5, positive electrodes including elemental sulfur as active materials were evaluated, whereas in Inventive Examples 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20, negative electrodes made of silicon materials were evaluated. [0049]

Tables 1 and 2 summarize the compositions of test cells in Inventive Examples 1 to 20 and Comparative Examples 1 to 5.

[0050]

(Table 1)

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	working	counter	solute	non-aqueous electrolyte
	electrode	electrode		
Inventive	sulfur	Li metal	Lin (CF ₃ S	room temperature
example 1			O_2) 2	molten salt 1(quaternary
		,		ammonium salt)
Comparative	sulfur	Li metal	LiPF ₆	EC/DEC
example 1				
Inventive	amorphous	L i metal	LiN (CF ₃ S	room temperature
example 2	silicon		O_2) 2	molten salt 1(quaternary
	thin			ammonium salt)
	film			
Inventive	sulfur	L i metal	LiPF ₆	fluorinated carbonate 1:
example 3				room temperature
				molten salt 1(quaternary
				ammonium salt)
Comparative	sulfur	Li metal	LiPF ₆	fluorinated carbonate 1
example 2			0	1
Inventive	amorphous	Li metal	LiPF ₆	fluorinated carbonate 1:
example 4	silicon		- - - - - - - - - - - -	room temperature
Champio	thin			molten salt 1(quaternary
	film			ammonium salt)
Inventive	sulfur	Li metal	Lin (CF ₃ S	room temperature
example 5	Surrur		0,),	molten salt 2(quaternary
evambre o				ammonium salt)
Inventive	amorphous	L i metal	LiN (CF ₃ S	room temperature
example 6	silicon		O_2) 2	molten salt 2(quaternary
example o	thin		0 27 2	ammonium salt)
	film			ammonium sait)
Inventive	sulfur	Li metal	LiN (CF ₃ S	room temperature
example 7	Surrur	L I metar	$\left(\begin{array}{ccc} C & 1 & 1 & 1 & 1 \\ O_2 & O_2 & O_2 & O_2 & O_2 & O_2 \end{array}\right)$	molten salt 3(quaternary
evambie i	}			ammonium salt)
Inventive	amorphous	Li metal	LiN (CF ₃ S	room temperature
example 8	silicon	L I metal	$\left(\begin{array}{ccc} C & C & C & C & C \\ O_2 & O_2 & O_2 & O_2 & O_2 & O_2 \end{array}\right)$	molten salt 3(quaternary
exambie o	thin			ammonium salt)
	I .			ammonitum sait/
T+:	film	L i metal	I i N (CE S	cyclic ether 1:
Inventive	sulfur	Li metal	LiN (CF ₃ S	
example 9			$O_2)_2$	room temperature molten salt 1(quaternary
				ammonium salt) = 50:50
Turnetine		T : mate1	LiN (CF ₃ S	cyclic ether 1:
Inventive	amorphous	Li metal		
example 10	silicon		$O_2)_2$	room temperature
	thin			molten salt 1(quaternary
	film	<u> </u>		ammonium salt) = 50 : 50

[0051]

(Table 2)

		Laguntan	solute	non-aqueous electrolyte
	working	counter	Solute	non aqueous electrolyte
	electrode	electrode		
Inventive	sulfur	Li metal	Lin (CF ₃ S	cyclic ether 1:
example 11			O_2	room temperature
				molten salt 1(quaternary
				ammonium salt) = 25:75
Inventive	amorphous	L i metal	LiN (CF ₃ S	cyclic ether 1:
example 12	silicon		O ₂) ₂	room temperature
,	thin			molten salt 1(quaternary
	film			ammonium salt) = 25:75
Comparative	sulfur	L i metal	LiN (CF ₃ S	cyclic ether 1
example 3		2 1		-
Inventive	sulfur	Li metal	O_2) 2 LiN (CF ₃ S	cyclic ether 2:
example 13			O_2) 2	room temperature
cxampic 10				molten salt 1(quaternary
				ammonium salt) = 50:50
T	1	T :	I : NI (O.D. O.	
Inventive	amorphous	Li metal	Lin (CF ₃ S	cyclic ether 2:
example 14	silicon	}	$O_2)_2$	room temperature
	thin			molten salt 1(quaternary
	film		,	ammonium salt) = 50:50
Inventive	sulfur	Li metal	LiN (CF ₃ S	cyclic ether 2:
example 15			O_2) 2	room temperature
				molten salt 1(quaternary
				ammonium salt) = 25:75
Inventive	amorphous	L i metal	Lin (CF ₃ S	cyclic ether 2:
example 16	silicon		O_2) 2	room temperature
	thin			molten salt 1(quaternary
	film			ammonium salt) = 25:75
Comparative	sulfur	L i metal	LiN (CF ₃ S	cyclic ether 2
example 4				
Inventive	sulfur	Li metal	O_2) 2 LiN(CF ₃ S	chain ether 1:
example 17	Surrar	D 1 MC CUI	$\left \begin{array}{c} C & C & C \\ C & C \end{array}\right _{2}$	room temperature
example 11				molten salt 1(quaternary
т		T	T : NI (O.D. O	ammonium salt) = 50 : 50
Inventive	amorphous	L i metal	Lin (CF ₃ S	chain ether 1:
example 18	silicon		$O_2)_2$	room temperature
	thin			molten salt 1(quaternary
	film			ammonium salt) = 50 : 50
Inventive	sulfur	Li metal	Lin (CF ₃ S	chain ether 1:
example 19			O_2) 2	room temperature
				molten salt l(quaternary
				ammonium salt) = 25:75
Inventive	amorphous	L i metal	LiN (CF ₃ S	chain ether 1:
example 20	silicon		O ₂) ₂	room temperature
•	thin		~ ~	molten salt 1(quaternary
	film			ammonium salt) = 25:75
Comparative	sulfur	L i metal	LiN (CF ₃ S	chain ether 1
example 5			O_2) 2	
CVGWhic o		J	2/ 2	<u> </u>

[0052]

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(Inventive Example 1)

In Inventive Example 1, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$, dissolved at a concentration of 0.3 mol/l in a room temperature molten salt, trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used.

For a positive electrode, 20% by weight of elemental sulfur, 70% by weight of acetylene black as conductive agent, and 10% by weight of polytetrafluoroethylene as binder were mixed, and the resultant mixture was ground in a mortar for 30 minutes, then pressed in a mold for five seconds under a pressure of 150 kg/cm² to give a disk-shaped material having a diameter of 10.3 mm. This material was wrapped in a net made of aluminum to be used as a positive electrode.

As shown in Fig. 1, the above-mentioned non-aqueous electrolyte 14 was poured into the test cell vessel 10, while the above-mentioned positive electrode was used for a working electrode 11, and lithium metal was used for each of a negative electrode as a counter electrode 12 and a reference electrode 13, to prepare a test cell of Inventive Example 1.

25 (Comparative Example 1)

In Comparative Example 1, a non-aqueous electrolyte including a lithium salt, LiPF₆ dissolved at a concentration of 1 mol/l in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) at a volume ratio of 1:1 was used. Otherwise, the test cell of Comparative Example 1 was prepared as in the case of the above-mentioned Inventive Example 1. [0056]

(Evaluation 1)

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Using the test cell of Inventive Example 1 prepared as shown above, the potential of the active electrode 11 (positive electrode) relative to the reference electrode 13 was scanned starting at an initial potential of 2.9 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for two cycles, at a scan rate of 0.5 mV/s in a scan range of 1.0 to 5.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 2.

Using the test cell of Comparative Example 1 prepared as shown above, the potential of the active electrode 11 (positive electrode) relative to the reference electrode 13 was scanned starting at an initial potential of 3.0 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for two cycles, at a scan rate of 0.5 mV/s in a scan range of 1.0 to 4.2 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 3.

[0058]

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As a result, in the case of the test cell of Inventive Example 1, an abrupt reduction current began to flow at around 2.3 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that the elemental sulfur was reduced. In addition, there were oxidation peaks between around 2.6 and 3.9 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized in this potential range. The same result was obtained also in the second cycle. It is therefore presumed that the reversible reaction of elemental sulfur was carried out.

In the case of the test cell of Comparative Example 1,

a reduction current began to flow at around 2.4 V or lower

(vs. Li/Li*) during scanning in the reduction direction, and

so it is presumed that the elemental sulfur was reduced.

However, there were no oxidation peaks during scanning in the

oxidation direction, and so it is presumed that the

20 above-mentioned reduced elemental sulfur was not oxidized.

In addition, a small amount of reduction current flowed at

around 2.4 V or lower (vs. Li/Li*) during scanning in the

oxidation direction. This is probably due to the reduction

of the residual elemental sulfur that was not reduced in the

earlier reaction.

[0060]

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The test cell of Inventive Example 1 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 2.7 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 4. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0061]

As a result, in the test cell of Inventive Example 1, the initial specific discharge capacity was approximately 654 mAh/g per 1 g of elemental sulfur, which was lower than the theoretical capacity of 1675 mAh/g, but the specific discharge capacity was markedly increased, compared with that of LiCoO₂ used as a general positive electrode. Moreover, the initial specific discharge capacity per 1 g of elemental sulfur exhibited a value as large as approximately 623 mAh/g, and the reversible reaction of elemental sulfur was also proved.

25 [0062]

Further, with this test cell of Inventive Example 1, the operation of discharging the cell to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charging the cell to a charge cutoff potential of 2.7 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the following equation. In Fig. 5, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle. [0063]

Charge-discharge efficiency = (Q_b/Q_a) x 100

As a result, in this test cell of Inventive Example 1, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 490 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 100%.

20 [0064]

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It is noted that in the test cell of Inventive Example 1, the average discharge voltage was approximately 2 V and the energy density per 1 g of elemental sulfur was approximately 980 mWh/g. The energy density was markedly increased, compared with the energy density per 1g of LiCoO₂

(approximately 540 mWh/g) used as a general positive electrode.

[0065]

(Inventive Example 2)

In Inventive Example 2, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 1 was used. As a working electrode 11, an amorphous silicon thin film formed by sputtering on a copper foil having an electrolytically treated surface and formed into a 2 cm x 2 cm size was used.

[0066]

A DC pulse sputtering apparatus was used. An argon (Ar) gas was used for atmospheric gas, and a 99.999% single silicon crystal for a target. The flow rate of the argon gas was set to 60 sccm, and the pressure of the sputtering atmosphere was set to 2 x 10^{-1} Pa. The electric power of sputtering was set to 2000 W (6.7 W/cm².)

[0067]

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The initial substrate temperature was set to 25°C. The 20 maximum temperature was approximately 100°C.

[0068]

As shown in Fig. 1, the above-mentioned non-aqueous electrolyte 14 was poured into the test cell vessel 10, while the above-mentioned working electrode 11 was used, and lithium metal was used for each of a counter electrode 12 and

a reference electrode 13, to prepare a test cell of Inventive Example 2.

[0069]

(Evaluation 1)

The test cell of Inventive Example 2 was discharged to a discharge cutoff potential of 0.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², and then charged to a charge cutoff potential of 2.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 6. Note that the solid line represents a charge curve showing the relationship between the potential and the active material per 1g of elemental sulfur during charging, and the broken line represents a discharge curve showing the relationship between the potential and the active material per 1 g of elemental sulfur during discharging.

[0070]

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As a result, in the test cell of Inventive Example 2, the initial specific charge and discharge capacities per 1 g of the active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used as a general negative electrode.

Moreover, the reversible reaction of elemental sulfur was also proved.

[0071]

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Further, with this test cell of Inventive Example 2, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 7, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

As a result, in this test cell of Inventive Example 2, the discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

20 [0073]

(Inventive Example 3)

In Inventive Example 3, a non-aqueous electrolyte including a lithium salt, LiPF_6 dissolved at a concentration of 1 mol/l in a mixed solvent of tetrafluoropropylene

carbonate and a quaternary ammonium salt, trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ at a volume ratio of 1:1 was used. Otherwise, test cell of Inventive Example 3 was prepared as in the case of the above-mentioned Inventive Example 1. [0074]

(Comparative Example 2)

In Comparative Example 2, a non-aqueous electrolyte including a lithium salt, LiPF₆ dissolved at a concentration of 1 mol/l in tetrafluoropropylene carbonate was used.

Otherwise, the test cell of Comparative Example 2 was prepared as in the case of the above-mentioned Inventive Example 1.

[0075]

(Evaluation 3)

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Using each of the test cells of Inventive Example 3 and Comparative Example 2 thus prepared, the electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 3.34 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 4.7 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The scanning operations were performed for four cycles in the test cell of Inventive Example 3, and for three cycles in the test cell of Comparative Example 2. The results of the test cell of

Inventive Example 3 are given in Fig. 8, and the results of the test cell of Comparative Example 2 are given in Fig. 9.

As a result, in the case of the test cell of Inventive

5 Example 3, a reduction current began to flow at around 2.3

V or lower (vs. Li/Li⁺) during scanning in the reduction
direction, and so it is presumed that elemental sulfur was
reduced. In addition, there were oxidation peaks between 2.0

and 3.0 V (vs. Li/Li⁺) during scanning in the oxidation

10 direction, and so it is presumed that the above-mentioned
reduced elemental sulfur was oxidized in this potential
range. The same result was obtained also in the second cycle.
It is therefore presumed that the reversible reaction of
elemental sulfur was carried out.

15 [0077]

In the case of the test cell of Comparative Example 2, a reduction current began to flow at around 2.2 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that the elemental sulfur was reduced.

20 However, there was an oxidation peak around 4.0 V (vs. Li/Li⁺) during scanning in the oxidation direction, and the energy efficiency was very poor. In the second cycle and thereafter, the oxidation peaks and the reduction currents abruptly decreased in size, and the resultant reversibility was poor.

25 [0078]

The discharge potential of elemental sulfur given by the results of the above-mentioned test cell of Inventive Example 3 was approximately 2.0 V (vs. Li/Li⁺), and the energy density of elemental sulfur converted from the theoretical specific capacity of 1675 mAh/g was 3350 Wh/g. The energy density was markedly increased, compared with that of LiCoO₂ (approximately 540 mWh/g) used in a general positive electrode.

[0079]

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10 (Inventive Example 4)

In Inventive Example 4, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 3 was used. Otherwise, the test cell of Example 3 was prepared as in the case of the above-mentioned Inventive Example 2. [0080]

(Evaluation 4)

The test cell of Inventive Example 4 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig.10. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line

represents a charge curve showing the relationship between the potential and capacity per 1 g of active material during discharging.

[0081]

As a result, in the test cell of Inventive Example 4, the initial specific charge and discharge capacities per 1 g of the active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general negative electrode.

Moreover, the reversible reaction of the silicon thin film was also proved.

[0082]

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Further, with this test cell of Inventive Example 4, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 11, the white circle and solid line represent the specific discharge capacity (mAh/g) in each cycle, and the triangle

and broken line represent the charge-discharge efficiency (%) in each cycle.

As a result, in the test cell of Inventive Example 4, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

10 (Inventive Example 5)

[0083]

[0084]

In Inventive Example 5, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in a room temperature molten salt, triethylmethylammonium

(Evaluation 5)

[0085]

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Using the test cell of Inventive Example 5 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 3.0 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three

cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 4.7 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 12.

As a result, in the case of the test cell of Inventive Example 5, a reduction current began to flow at around 2.3 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that elemental sulfur was reduced. In addition, there was an oxidation peak around 3.8 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at around this potential. The same results were obtained also in the second cycle and thereafter. It is therefore presumed that the reversible reaction of elemental sulfur was carried out.

The test cell of Inventive Example 5 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.5 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 13. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1g of elemental sulfur during discharging, and the broken line

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represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[8800]

As a result, in the test cell of Inventive Example 5, the initial specific discharge capacity per 1 g of elemental sulfur was approximately 1138 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode.

10 [0089]

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(Inventive Example 6)

In Inventive Example 6, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 5 was used. Otherwise, the test cell of Example 6 was prepared as in the case of the above-mentioned Inventive Example 2. [0090]

(Evaluation 6)

Using the test cell of Inventive Example 6 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.6 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 0.0 to 2.75 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 14.

[0091]

As a result, in the case of the test cell of Example 6, there was a reduction peak around 0.03 V (vs. Li/Li⁺) during scanning in the reduction direction, and there was an 5 oxidation peak around 0.7 V (vs. Li/Li+) during scanning in the oxidation direction. It is presumed that insertion/release of lithium into/from silicon occurred at around this potential. The same results were obtained in the second cycle and thereafter, and so it is presumed that the reversible reaction of silicon with lithium was carried out. [0092]

(Inventive Example 7)

In Inventive Example 7, a non-aqueous electrolyte including a lithium salt, LiN(CF₃SO₂)₂ dissolved at a concentration of 0.5 mol/l in a room temperature molten salt, trimethylhexylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_6H_{13})N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell of Inventive Example 7 was prepared as in the case of the above-mentioned test cell of Inventive Example 1.

[0093] 20

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(Evaluation 7)

Using the test cell of Inventive Example 7 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.8 V (vs. Li/Li⁺) in a reduction

direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 4.7 V (vs. Li/Li^+), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 15.

5 [0094]

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As a result, in the case of the test cell of Inventive Example 7, a reduction current began to flow at around 2.3 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that the elemental sulfur was reduced. In addition, there was an oxidation peak around 2.6 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at around this potential. The same results were obtained also in the second cycle and thereafter. It is therefore presumed that the reversible reaction of elemental sulfur was carried out.

Further, the test cell of Inventive Example 7 was discharged to a discharge cutoff potential of 1.0 V (vs. 20 Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.5 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 16. Note that the solid line represents a discharge curve showing the relationship between the potential and the

capacity per 1g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

5 [0096]

As a result, in the test cell of Example 7, the initial specific discharge capacity per 1 g of elemental sulfur was 588 mAh/g, and the specific discharge capacity was markedly increased, compared with that of LiCoO_2 used in a general positive electrode.

[0097]

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(Inventive Example 8)

In Inventive Example 8, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 7 was used. Otherwise, the test cell of Example 8 was prepared as in the case of the above-mentioned Inventive Example 2. [0098]

(Evaluation 8)

The test cell of Inventive Example 8 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig.17. Note that the solid line represents a discharge curve showing the

relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and capacity per 1 g of active material during discharging.

[0099]

[0100]

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As a result, in the test cell of Example 8, the initial specific charge and discharge capacities per 1 g of active material were 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general positive electrode. Moreover, the reversible reaction of the silicon thin film was also proved.

Further, with the test cell of Inventive Example 8, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 18, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken

line represent the charge-discharge efficiency (%) in each cycle.

[0101]

As a result, in the test cell of Inventive Example 8, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

[0102]

10 (Inventive Example 9)

In Inventive Example 9, a non-aqueous electrolyte including a lithium salt, or $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in a mixture of 50% by volume of 1,3-dioxolane and 50% by volume of trimethylpropylammonium bis (trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell of Inventive Example 9 was prepared as in the case of the above-mentioned Inventive Example 1.

[0103]

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20 (Evaluation 9)

Using the test cell of Inventive Example 9 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.4 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three

cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 19.

As a result, in the case of the test cell of Inventive Example 9, a reduction current began to flow at around 2.3 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that elemental sulfur was reduced. In addition, there was an oxidation peak around 2.6 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at around this potential. The same results were obtained also in the second cycle and thereafter. It is therefore presumed that the reversible reaction of elemental sulfur was carried out.

[0105]

The test cell of Inventive Example 9 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 20. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line

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represents a charge curve showing the relationship between the potential and capacity per 1 g of elemental sulfur during charging.

[0106]

As a result, in the test cell of Inventive Example 9, the initial specific discharge capacity per 1 g of elemental sulfur was 2230 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode. Further, the mixture of 1,3-dioxolane and trimethylpropylammonium bis

(trifluoromethylsulfonyl)imide ((CH₃) $_3$ N⁺(C₃H₇)N⁻(SO₂CF₃) $_2$) increases the specific capacities at around 2.0 V or higher during discharging, compared with that obtained using 1,3-dioxolane alone, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium bis (trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ alone as an electrolyte, as shown in Inventive Example 1.

[0107]

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20 (Inventive Example 10)

In Inventive Example 10, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 9 was used. Otherwise, the test cell in Inventive Example 10 was prepared as in the case of the test cell of the above-mentioned Inventive Example 2.

[0108]

(Evaluation 10)

The test cell of Inventive Example 10 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 21. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of active material during discharging.

15 [0109]

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As a result, in the test cell of Inventive Example 10, the initial specific charge and discharge capacities per 1 g of active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general positive electrode. The reversible reaction of the silicon thin film was also proved.
[0110]

Further, with this test cell of Inventive Example 10, 25 the operation of charging the cell to a charge cutoff

potential of 0.0 V (vs. Li/Li^+) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li^+) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 22, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

[0111]

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As a result, in the test cell in Inventive Example 10, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge/discharge efficiencies were also kept constant at approximately 94%.

[0112]

(Inventive Example 11)

In Inventive Example 11, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in a mixture of 25% by volume of 1,3-dioxolane and 75% by volume of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide

25 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell

of Inventive Example 11 was prepared as in the case of the above-mentioned Inventive Example 1.

(Evaluation 11)

[0113]

Using the test cell of Inventive Example 11 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.4 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.3 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 23.

As a result, in the case of the test cell of Inventive

Example 11, a reduction peak appeared at around 1.9 V (vs.
Li/Li⁺) during scanning in the reduction direction, and so
it is presumed that the elemental sulfur was reduced. In
addition, an oxidation peak appeared around 2.4 V (vs. Li/Li⁺)
during scanning in the oxidation direction, and so it is
presumed that the above-mentioned reduced elemental sulfur
was oxidized at around this potential. Also in the second
cycle and thereafter, there were reduction peaks at around
1.5 V (vs. Li/Li⁺) during scanning in the reduction direction,
and oxidation peaks at around 2.4 V (vs. Li/Li⁺) during
scanning in the oxidation direction. It is therefore presumed

that the reversible reaction of elemental sulfur was carried out.

[0115]

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Further, the test cell of Inventive Example 11 was discharged to a discharge cutoff potential of 1.0 V (vs. 5 Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm^2 , to examine the initial charge-discharge characteristics. The results are given in Fig. 24. Note that the solid line represents a discharge curve 10 showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 q 15 of elemental sulfur during charging. [0116]

As a result, in the test cell of Inventive Example 11, the initial specific discharge capacity per 1 g of elemental sulfur was 2291 mAh/g, and the specific discharge capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode. Further, the mixture of

 ${\tt 1,3-dioxolane} \ {\tt and} \ {\tt trimethylpropylammonium}$

bis(trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ increased the capacity at around 25 2.0 V or higher (vs. Li/Li⁺) during discharging, compared with

that obtained using 1,3-dioxolane alone as an electrolyte, as shown in Comparative Example 3 below, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2) \text{ alone as an electrolyte, as shown in Inventive Example 1.}$

[0117]

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(Inventive Example 12)

In Inventive Example 12, the same non-aqueous

10 electrolyte as that in the above-mentioned Inventive Example
11 was used. Otherwise, the test cell of Inventive Example
12 was prepared as in the case of the above-mentioned
Inventive Example 2.

[0118]

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15 (Evaluation 12)

The test cell of Inventive Example 12 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 25. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between

the potential and the capacity per 1 g of active material during discharging.

[0119]

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As a result, in this test cell of Inventive Example 12, the initial specific charge and discharge capacities per 1 g of active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general negative electrode. The reversible reaction of the silicon thin film was also proved.

[0120]

Further, with the test cell of Inventive Example 12, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 26, the solid line and white circle represent the discharge capacity (mAh/g) in each cycle, and the broken line and triangle represent the charge-discharge efficiency (%) in each cycle.

25 [0121]

As a result, in this test cell of Inventive Example 12, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

[0122]

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(Comparative Example 3)

In Comparative Example 3, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in 1,3-dioxolane was used. Otherwise, the test cell of Comparative Example 3 was prepared as in the case of the above-mentioned Inventive Example 1. [0123]

(Evaluation 13)

Using the test cell of Comparative Example 3 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.2 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 27.

[0124]

As a result, in the case of the test cell of Comparative 25 Example 3, a reduction peak appeared at around 1.8 V (vs.

Li/Li⁺) during scanning in the reduction direction, and a large reduction current flowed at around 1.2 V or lower (vs. Li/Li⁺). It is thus presumed that the elemental sulfur was reduced. In addition, there was an oxidation peak at around 2.6 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at around this potential.

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[0126]

The test cell of Comparative Example 3 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 28.

Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0127]

As a result, in this test cell of Comparative Example 3, the initial specific discharge capacity per 1 g of elemental sulfur was 1677 mAh/g. The specific discharge

capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode, while the discharge potential was as low as approximately 1.2 V (vs. Li/Li⁺).
[0128]

5 (Evaluation 14)

The mixture of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2) \text{ and } 1,3-\text{dioxolane has reduced}$ viscosity in the electrolyte, compared with the electrolyte containing only trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2). \text{ Accordingly, the mixture is }$ preferable for use as an electrolyte. [0129]

15 (Evaluation 15)

The results of Inventive Examples 1, 9, 11, and Comparative Example 3 show that in the use of a positive electrode including elemental sulfur, it is more preferable to mix trimethylpropylammonium

bis (trifluoromethylsulfonyl) imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2) \text{ with } 1,3-\text{dioxolane than to use} \\ 1,3-\text{dioxolane or trimethylpropylammonium} \\ \text{bis (trifluoromethylsulfonyl) imide} \\ ((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2) \text{ alone, when comparing the specific} \\ \text{25 discharge capacities at around 2 V or higher (vs. Li/Li^+)}$

during discharging. The 1,3-dioxolane may be set in the range of 0.1 to 99.9% by volume. Preferably, the ratio of 1,3-dioxolane may be set in the range of 0.1 to 50% by volume, more preferably in the range of 0.1 to 25% by volume.

5 [0130]

(Inventive Example 13)

In Inventive Example 13, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in a mixture of 50% by volume of tetrahydrofuran and 50% by volume of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell of Inventive Example 13 was prepared as in the case of the above-mentioned Inventive Example 1.

15 [0131]

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(Evaluation 16)

Using the test cell of Inventive Example 13 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.5 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 29.

25 [0132]

As a result, in the case of the test cell of Inventive Example 13, reduction peaks appeared at around 2.0 V (vs. Li/Li⁺) and 1.5 V (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that the elemental sulfur was reduced. In addition, an oxidation current flowed at around 2.2 V or higher (vs. Li/Li⁺) during scanning in the oxidation direction, and it is presumed that the above-mentioned reduced elemental sulfur was oxidized at this potential range.

10 [0133]

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Further, the test cell of Inventive Example 12 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 30. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0134]

As a result, in this test cell of Inventive Example 13, 25 the initial specific discharge capacity per 1 g of elemental

sulfur was 1479 mAh/g. The specific discharge capacity was markedly increased, compared with that of $LiCoO_2$ used in a general positive electrode. In addition, the mixture of tetrahydrofuran and trimethylpropylammonium

5 bis(trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ increased the capacity at around 2.0 V or higher (vs. Li/Li⁺) during discharging, compared with that obtained using tetrahydrofuran alone as an electrolyte, as shown in Comparative Example 4 below, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ alone as an electrolyte, as shown in Inventive Example 1.

[0135]

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15 (Inventive Example 14)

In Inventive Example 14, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 13 was used. Otherwise, the test cell of Inventive Example 14 was prepared as in the case of the above-mentioned Inventive Example 2.

[0136]

(Evaluation 17)

The test cell of Inventive Example 14 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge

cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 31. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of active material during discharging.

10 [0137]

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As a result, in this test cell of Inventive Example 14, the initial specific charge and discharge capacities per 1 g of active material were 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general negative electrode. The reversible reaction of the silicon thin film was also proved.

Further, with the test cell of Inventive Example 14, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find

out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 32, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

[0139]

[0140]

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As a result, in this test cell of Inventive Example 14, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

(Inventive Example 15)

In Inventive Example 15, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in a mixture of 25% by volume of tetrahydrofuran and 75% by volume of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide

20 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell of Inventive Example 15 was prepared as in the case of the above-mentioned Inventive Example 1.

[0141]

(Evaluation 18)

Using the test cell of Inventive Example 15 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.6 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 33.

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As a result, in the case of the test cell of Inventive Example 15, a reduction current flowed at around 2.4 V or lower (vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that elemental sulfur was reduced. In addition, an oxidation peak appeared at around 2.5 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at around this potential.

[0143]

The test cell of Inventive Example 15 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 34. Note that the solid line represents a discharge curve showing the

relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0144]

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As a result, in this test cell of Inventive Example 14, the initial specific discharge capacity per 1 g of elemental sulfur was 1547 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode. Further, the mixture of tetrahydrofuran and trimethylpropylammonium bis(trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ increased the capacity at around 2.0~V or higher (vs. Li/Li⁺) during discharging, compared with that obtained using tetrahydrofuran alone as an electrolyte, as shown in Comparative Example 4 below, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ alone as an electrolyte, as shown in Inventive Example 1.

[0145]

(Inventive Example 16)

In Inventive Example 16, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example

15 was used. Otherwise, the test cell of Inventive Example
16 was prepared as in the case of the above-mentioned
Inventive Example 2.

[0146]

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5 (Evaluation 19)

The test cell of Inventive Example 16 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 35. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of active material during discharging.

[0147]

As a result, in this test cell of Inventive Example 16,

20 the initial specific charge and discharge capacities per 1

g of active material were approximately 3417 mAh/g and 2989

mAh/g, respectively. The specific charge/discharge capacity

was markedly increased, compared with that of a carbon

material used in a general negative electrode. The reversible

25 reaction of the silicon thin film was also proved.

[0148]

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Further, with the test cell of Inventive Example 16, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 36, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

15 [0149]

As a result, in this test cell of Inventive Example 16, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

[0150]

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(Comparative Example 4)

In Comparative Example 4, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in tetrahydrofuran was used.

Otherwise, the test cell of Comparative Example 4 was prepared as in the case of the above-mentioned Inventive Example 1.
[0151]

(Evaluation 20)

Using the test cell of Comparative Example 4 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.3 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 37.

As a result, in the case of the test cell of Comparative

Example 4, a reduction peak appeared at around 1.6 V (vs.

Li/Li+), and a large reduction current flowed at around 1.2

V or lower (vs. Li/Li+) during scanning in the reduction

direction, and so it is presumed that elemental sulfur was

reduced. In addition, there was an oxidation peak at around

20 2.5 V (vs. Li/Li+) during scanning in the oxidation direction,

and it is presumed that the above-mentioned reduced elemental

sulfur was oxidized at around this potential.

[0153]

Further, the test cell of Comparative Example 4 was 25 discharged to a discharge cutoff potential of 1.0 V (vs.

Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.3 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 38. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0154]

As a result, in this test cell of Comparative Example 4, the initial specific discharge capacity per 1 g of elemental sulfur was 1065 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO_2 used in a general positive electrode, while the discharge potential was as low as approximately 1.2 V (vs. Li/Li^+). [0155]

(Evaluation 21)

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 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$. Accordingly, the mixture is preferable for use as an electrolyte. [0156]

(Evaluation 22)

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Further, the results of Inventive Examples 1, 13, 17, and Comparative Example 4 show that in the use of a positive electrode including elemental sulfur, it is preferable to mix trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ with tetrahydrofuran than to use trimethylpropylammonium bis(trifluoromethylsulfonyl)imide 10 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ or tetrahydrofuran alone, when comparing the specific discharge capacities in plateaus at around 2.0 V or higher (vs. Li/Li⁺) in the discharge characteristics. The tetrahydrofuran may be set in the range of 0.1 to 99.9% by volume. Preferably, the ratio of 15 tetrahydrofuran may be set in the range of 0.1 to 50% by volume, more preferably, in the range of 0.1 to 25% by volume. [0157]

(Inventive Example 17)

In Inventive Example 17, a non-aqueous electrolyte 20 including a lithium salt, LiN(CF3SO2)2 dissolved at a concentration of 0.5 mol/l in a mixture of 50% by volume of 1,2-dimethoxyethane and 50% by volume of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ was used. Otherwise, the test cell 25

of Inventive Example 17 was prepared as in the case of the above-mentioned Inventive Example 1.

[0158]

(Evaluation 23)

Using the test cell of Inventive Example 17 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.8 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.0 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 39.

As a result, in the case of the test cell of Inventive

Example 17, a reduction peak appeared at around 2.0 V (vs.

Li/Li+) during scanning in the reduction direction, and so

it is presumed that the elemental sulfur was reduced. In

addition, an oxidation current flowed at around 2.2 V or

higher (vs. Li/Li+) during scanning in the oxidation

direction, and so it is presumed that the above-mentioned

reduced elemental sulfur was oxidized at this potential

range.

[0160]

Further, the test cell of Inventive Example 17 was 25 discharged to a discharge cutoff potential of 1.0 V (vs.

Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 40. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

[0161]

As a result, in this test cell of Inventive Example 17, the initial specific discharge capacity per 1 g of elemental sulfur was 1919 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO_2 used in a general positive electrode. Further, the mixture of tetrahydrofuran and trimethylpropylammonium

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ increased the specific capacity at around 1.5 V or higher (vs. Li/Li⁺) during discharging, compared with that obtained using tetrahydrofuran alone as an electrolyte, as shown in Comparative Example 5, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium

25 bis(trifluoromethylsulfonyl)imide

bis(trifluoromethylsulfonyl)imide

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 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ alone as an electrolyte, as shown in Inventive Example 1. [0162]

(Inventive Example 18)

In Inventive Example 18, the same non-aqueous electrolyte as that in the above-mentioned Inventive Example 17 was used. Otherwise, the test cell of Inventive Example 18 was prepared as in the case of the above-mentioned Inventive Example 2.

10 [0163]

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(Evaluation 24)

The test cell of Inventive Example 18 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 41. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of active material during discharging.

[0164]

As a result, in this test cell of Inventive Example 18, the initial specific charge and discharge capacities per 1 g of active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a negative electrode. The reversible reaction of the silicon thin film was also proved.

[0165]

Further, with the test cell of Inventive Example 18, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 42, the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

[0166]

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As a result, in this test cell of Inventive Example 18, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g,

and the charge-discharge efficiencies were also kept constant at approximately 94%.

[0167]

(Inventive Example 19)

In Inventive Example 19, a non-aqueous electrolyte including a lithium salt, LiN(CF₃SO₂)₂ dissolved at a concentration of 0.5 mol/l in a mixture of 25% by volume of 1,2-dimethoxyethane and 75% by volume of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide ((CH₃)₃N⁺(C₃H₇)N⁻(SO₂CF₃)₂) was used. Otherwise, the test cell of Inventive Example 19 was prepared as in the case of the above-mentioned Inventive Example 1.

(Evaluation 25)

Using the test cell of Inventive Example 19 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.4 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to 3.3 V (vs. Li/Li⁺), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 43.

As a result, in the case of the test cell of Inventive 25 Example 19, a reduction current flowed at around 2.4 V or lower

(vs. Li/Li⁺) during scanning in the reduction direction, and so it is presumed that elemental sulfur was reduced. In addition, an oxidation peak appeared at around 2.5 V (vs. Li/Li⁺) during scanning in the oxidation direction, and so it is presumed that the above-mentioned reduced elemental sulfur was oxidized at this potential range.

Further, the test cell of Inventive Example 19 was discharged to a discharge cutoff potential of 1.0 V (vs. Li/Li⁺) at a discharge current of 0.13 mA/cm², and then charged to a charge cutoff potential of 3.0 V (vs. Li/Li⁺) at a charge current of 0.13 mA/cm², to examine the initial charge-discharge characteristics. The results are given in Fig. 44. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during discharging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of elemental sulfur during charging.

20 [0171]

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As a result, in this test cell of Inventive Example 19, the initial specific discharge capacity per 1 g of elemental sulfur was 1636 mAh/g. The specific discharge capacity was markedly increased, compared with that of $LiCoO_2$ used in a general positive electrode. Further, the mixture of

tetrahydrofuran and trimethylpropylammonium bis(trifluoromethylsulfonyl)imide

 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ increased the specific capacity at around 1.5 V or higher (vs. Li/Li⁺) during discharging,

5 compared with that obtained using 1,2-dimethoxyethane alone as an electrolyte, as shown in Comparative Example 5 below, and the specific discharge capacity was also greater than that obtained using trimethylpropylammonium

bis(trifluoromethylsulfonyl)imide

10 $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2)$ alone as an electrolyte, as shown in Inventive Example 1.

[0172]

(Inventive Example 20)

In Inventive Example 20, the same non-aqueous

electrolyte as that in the above-mentioned Inventive Example

19 was used. Otherwise, the test cell of Inventive Example

20 was prepared as in the case of the above-mentioned

Inventive Example 2.

[0173]

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20 (Evaluation 26)

The test cell of Inventive Example 20 was charged to a charge cutoff potential of 0.0 V (vs. Li/Li^+) at a charge current of 0.05 mA/cm², and then discharged to a discharge cutoff potential of 2.0 V (vs. Li/Li^+) at a discharge current of 0.05 mA/cm², to examine the initial charge-discharge

characteristics. The results are given in Fig. 45. Note that the solid line represents a discharge curve showing the relationship between the potential and the capacity per 1 g of active material during charging, and the broken line represents a charge curve showing the relationship between the potential and the capacity per 1 g of active material during discharging.

[0174]

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As a result, in this test cell of Inventive Example 20, the initial specific charge and discharge capacities per 1 g of active material were approximately 3417 mAh/g and 2989 mAh/g, respectively. The specific charge/discharge capacity was markedly increased, compared with that of a carbon material used in a general negative electrode. The reversible reaction of the silicon thin film was also proved.

Further, with the test cell of Inventive Example 20, the operation of charging the cell to a charge cutoff potential of 0.0 V (vs. Li/Li⁺) at a charge current of 0.05 mA/cm², and then discharging the cell to a discharge cutoff potential of 2.0 V (vs. Li/Li⁺) at a discharge current of 0.05 mA/cm² was repeated, to measure the charge capacity Q_a (mAh/g) and discharge capacity Q_b (mAh/g) in each cycle, and also find out the charge-discharge efficiency (%) in each cycle in accordance with the above-mentioned equation. In Fig. 46,

the white circle and solid line represent the discharge capacity (mAh/g) in each cycle, and the triangle and broken line represent the charge-discharge efficiency (%) in each cycle.

5 [0176]

As a result, in this test cell of Inventive Example 20, the specific discharge capacities in the third cycle and thereafter were kept constant at approximately 3243 mAh/g, and the charge-discharge efficiencies were also kept constant at approximately 94%.

[0177]

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(Comparative Example 5)

In Comparative Example 5, a non-aqueous electrolyte including a lithium salt, $LiN(CF_3SO_2)_2$ dissolved at a concentration of 0.5 mol/l in 1,2-dimethoxyethane was used. Otherwise, the test cell of Comparative Example 5 was prepared as in the case of the above-mentioned Inventive Example 1. [0178]

(Evaluation 27)

Using the test cell of Comparative Example 5 thus prepared, the potential of the active electrode 11 relative to the reference electrode 13 was scanned starting at an initial potential of 2.4 V (vs. Li/Li⁺) in a reduction direction, and then in an oxidation direction for three cycles, at a scan rate of 1.0 mV/s in a scan range of 1.0 to

3.0 V (vs. Li/Li^+), to measure the cyclic voltammetry in each cycle. The results are given in Fig. 47.

As a result, in the case of the test cell of Comparative

5 Example 5, a reduction peak appeared at around 1.8 V (vs.
Li/Li+) and a large reduction current flowed at around 1.2
V or lower (vs. Li/Li+) during scanning in the reduction
direction, and so it is presumed that elemental sulfur was
reduced. In addition, there was an oxidation peak at around

10 2.5 V (vs. Li/Li+) during scanning in the oxidation direction,
and so it is presumed that the above-mentioned reduced
elemental sulfur was oxidized at around this potential.

[0180]

Further, the test cell of Comparative Example 5 was

discharged to a discharge cutoff potential of 1.0 V (vs.

Li/Li+) at a discharge current of 0.13 mA/cm2, and then charged
to a charge cutoff potential of 3.0 V (vs. Li/Li+) at a charge
current of 0.13 mA/cm2, to examine the initial
charge-discharge characteristics. The results are given in

Fig. 48. Note that the solid line represents a discharge curve
showing the relationship between the potential and the
capacity per 1 g of elemental sulfur during discharging, and
the broken line represents a charge curve showing the
relationship between the potential and the capacity per 1 g

of elemental sulfur during charging.

[0181]

As a result, in this test cell of Comparative Example 5, the initial specific discharge capacity per 1 g of elemental sulfur was 1921 mAh/g. The specific discharge capacity was markedly increased, compared with that of LiCoO₂ used in a general positive electrode. However, the capacity at around 2 V or higher (vs. Li/Li⁺) was small in the discharge characteristics, and most of the discharge potentials were as low as approximately 1.2 V (vs. Li/Li⁺).

10 [0182]

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[0183]

(Evaluation 28)

The mixture of trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2) \text{ and } 1,2-\text{dimethoxyethane has}$ reduced viscosity in the electrolyte, compared with the electrolyte containing only trimethylpropylammonium bis(trifluoromethylsulfonyl)imide $((CH_3)_3N^+(C_3H_7)N^-(SO_2CF_3)_2). \text{ Accordingly, the mixture is preferable for use as an electrolyte.}$

(Evaluation 29)

Moreover, the results of Inventive Examples 1, 17, 19, and Comparative Example 5 show that in the use of a positive electrode including elemental sulfur, it is more preferable to mix trimethylpropylammonium

bis(trifluoromethylsulfonyl)imide

((CH₃)₃N⁺(C₃H₇)N⁻(SO₂CF₃)₂) with 1,2-dimethoxyethane than to

use trimethylpropylammonium

bis(trifluoromethylsulfonyl)imide

((CH₃)₃N⁺(C₃H₇)N⁻(SO₂CF₃)₂) or 1,2-dimethoxyethane alone, when

comparing the specific discharge capacities at around 1.5 V

or higher (vs. Li/Li⁺) in the discharge characteristics. The

1,2-dimethoxyethane may be set in the range of 0.1 to 99.9%

by volume. Preferably, the ratio of 1,2-dimethoxyethane may

be set in the range of 0.1 to 50% by volume, more preferably,

in the range of 0.1 to 25% by volume.

[0184]

The results above show that increased specific discharge capacity can be obtained by mixing a quaternary ammonium salt, such as trimethylpropylammonium bis(trifluoromethylsulfonyl)imide ((CH₃)₃ N⁺ (C₃ H₇)N⁻ (SO₂ CF₃)₂), trimethyloctylammonium bis(trifluoromethylsulfonyl)imide ((CH₃)₃N⁺(C₈H₁₇)N⁻(SO₂CF₃)₂), trimethylallylammonium bis(trifluoromethylsulfonyl)imide ((CH₃)₃N⁺(Allyl)N⁻(SO₂CF₃)₂), trimethylammonium bis(trifluoromethylsulfonyl)imide ((CH₃)₃N⁺(C₆H₁₃)N⁻(SO₂CF₃)₂), trimethylethylammonium 2,2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide

```
((CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>(C<sub>2</sub>H<sub>5</sub>)(CF<sub>3</sub>CO)N<sup>-</sup>(SO<sub>2</sub>CF<sub>3</sub>)), trimethylallylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((CH_3)_3N^+(Allyl)(CF_3CO)N^-(SO_2CF_3)), trimethylpropylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
   ((CH_3)_3N^+(C_3H_7)(CF_3CO)N^-(SO_2CF_3)), tetraethylammonium
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    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((C_2H_5)_4N^+(CF_3CO)N^-(SO_2CF_3)), or triethylmethylammonium
    2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide
    ((C_2H_5)_3N^+(CH_3)(CF_3CO)N^-(SO_2CF_3)); or a room temperature
    molten salt having a melting point of not higher than 60°C,
10
    such as an imidazolium salt illustrated by
    1-ethyl-3-methylimidazolium
    bis (pentafluoroethylsulfonyl) imide
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2C_2F_5)_2),
15
    1-ethyl-3-methylimidazolium
    bis(trifluoromethylsulfonyl)imide
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)N^-(SO_2CF_3)_2),
    1-ethyl-3-methylimidazolium tetrafluoroborate
    ((C_2H_5)(C_3H_3N_2)^+(CH_3)BF_4^-), 1-ethyl-3-methylimidazolium
    pentafluoroborate ((C_2H_5)(C_3H_3N_2)^+(CH_3)PF_6^-) with at least one
20
    type of an organic solvent selected from fluorinated cyclic
    carbonates, such as trifluoropropylene carbonate and
    fluoroethyl carbonate; cyclic ethers, such as 1,3-dioxolane,
    4-methyl-1,3-dioxolane, tetrahydrofuran, 2-methyl
    tetrahydrofuran, propylene oxide, 1,2-butylene oxide,
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1,4-dioxane, 1,3,5-trioxane, furan, 2-methylfuran, 1,8-cineole, and crown ether; or chain ethers, such as 1,2-dimethoxyethane, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, ethyl vinyl ether, butyl vinyl ether, methyl phenyl ether, ethyl phenyl 5 ether, butyl phenyl ether, pentyl phenyl ether, methoxytoluene, benzyl ethyl ether, diphenyl ether, dibenzyl ether, o-dimethoxybenzene, 1,2-diethoxyethane, 1,2-dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, diethylene glycol dibutyl 10 ether, 1,1-dimethoxymethane, 1,1-diethoxyethane, triethylene glycol dimethyl ether, and tetraethylene glycol dimethyl ether. Needless to say, a mixture of at least two types of room temperature molten salts having a melting point of not higher than 60°C may also be used. 15

[FIG. 1]

[Brief Description of the Drawings]

A schematic diagram for use in explaining a test cell prepared in each of Inventive Examples 1 to 20 and Comparative Examples 1 to 5 of this invention

[FIG. 2]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the potential of the working electrode in the test cell of Inventive Example 1

25 [FIG. 3]

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A diagram showing the cyclic voltammetry of a working electrode measured by scanning the potential of the working electrode in the test cell of Comparative Example 1

[FIG. 4]

A diagram showing initial charge-discharge characteristics of the test cell of Inventive Example 1 [FIG. 5]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 1 was repeatedly charged/discharged

[FIG. 6]

A diagram showing initial charge-discharge characteristics of the test cell of Inventive Example 2

15 [FIG. 7]

10

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 2 was repeatedly charged/discharged

20 [FIG. 8]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the potential of the working electrode in the test cell of Inventive Example 3

[FIG. 9]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the potential of the working electrode in the test cell of Comparative Example 2

[FIG. 10]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 4 [FIG. 11]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 5 was repeatedly charged/discharged

[FIG. 12]

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A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 5

[FIG. 13]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 5 [FIG. 14]

20 A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 6

[FIG. 15]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 7

[FIG. 16]

A diagram showing initial charge/discharge

characteristics of the test cell of Inventive Example 7

[FIG. 17]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 8 [FIG. 18]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 8 was repeatedly charged/discharged

15 [FIG. 19]

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A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 9

[FIG. 20]

20 A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 9 [FIG. 21]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 10 [FIG. 22]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 10 was repeatedly charged/discharged

5 [FIG. 23]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 11

[FIG. 24]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 11 [FIG. 25]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 12 [FIG. 26]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 12 was repeatedly charged/discharged

20 [FIG. 27]

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A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Comparative Example 3

[FIG. 28]

A diagram showing initial charge/discharge characteristics of the test cell of Comparative Example 3 [FIG. 29]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 13

[FIG. 30]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 13

[FIG. 31]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 14 [FIG. 32]

A diagram showing the discharge capacity and

15 charge-discharge efficiency in each cycle obtained when the
test cell of Inventive Example 14 was repeatedly
charged/discharged

[FIG. 33]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 15

[FIG. 34]

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A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 15 [FIG. 35]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 16 [FIG. 36]

A diagram showing the discharge capacity and

5 charge-discharge efficiency in each cycle obtained when the
test cell of Inventive Example 16 was repeatedly
charged/discharged

[FIG. 37]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Comparative Example 4

[FIG. 38]

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A diagram showing initial charge/discharge characteristics of the test cell of Comparative Example 4 [FIG. 39]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 17

[FIG. 40]

20 A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 17 [FIG. 41]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 18 [FIG. 42]

Fig 42 is a diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 18 was repeatedly charged/discharged

5 [FIG. 43]

A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Inventive Example 19

[FIG. 44]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 19
[FIG. 45]

A diagram showing initial charge/discharge characteristics of the test cell of Inventive Example 20 [FIG. 46]

A diagram showing the discharge capacity and charge-discharge efficiency in each cycle obtained when the test cell of Inventive Example 20 was repeatedly charged/discharged

20 [FIG. 47]

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A diagram showing the cyclic voltammetry of a working electrode measured by scanning the working electrode in the test cell of Comparative Example 5

[FIG. 48]

A diagram showing initial charge/discharge characteristics of the test cell of Comparative Example 5 [Description of Reference Numerals]

- 10 Test cell vessel
- 5 11 Working electrode
 - 12 Counter electrode
 - 13 Reference electrode
 - 14 Non-aqueous electrolyte

10

Fig. 1

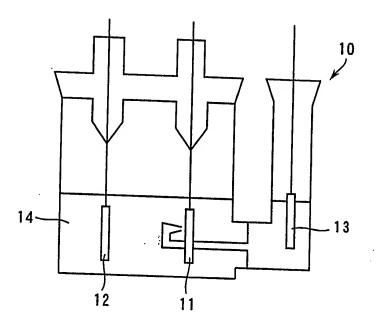
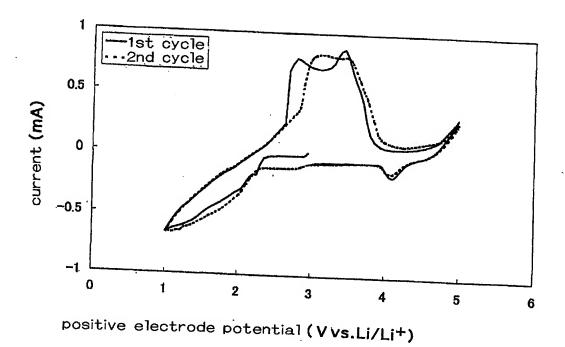
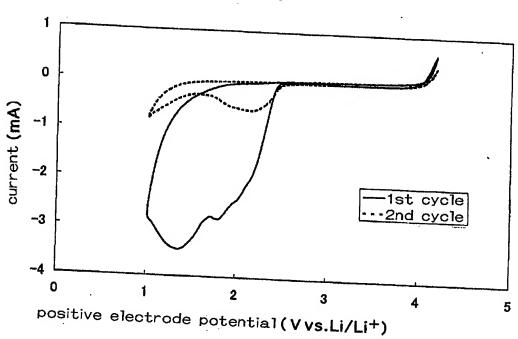
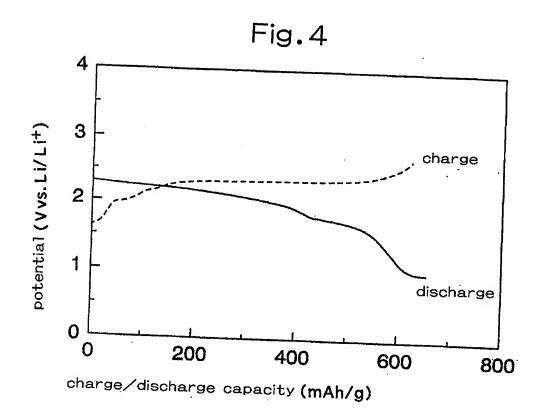


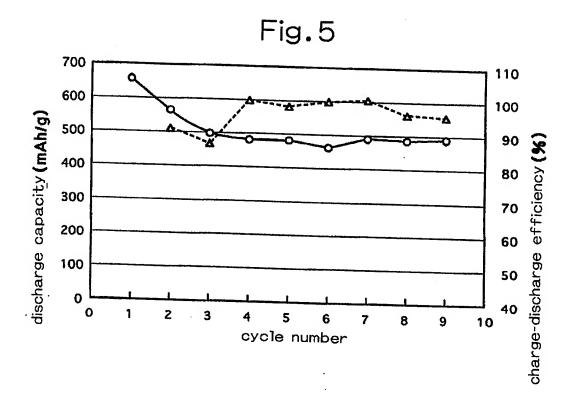
Fig.2

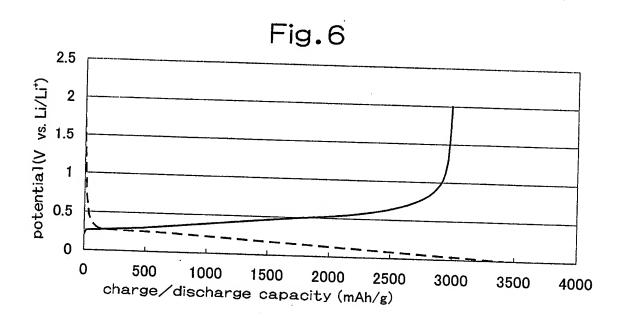


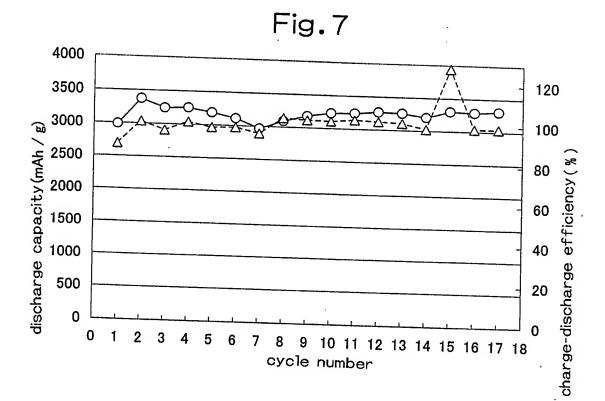


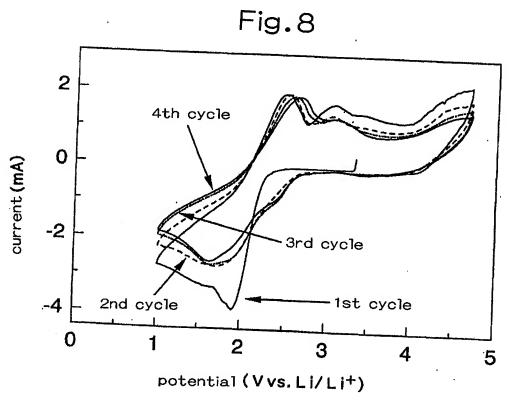


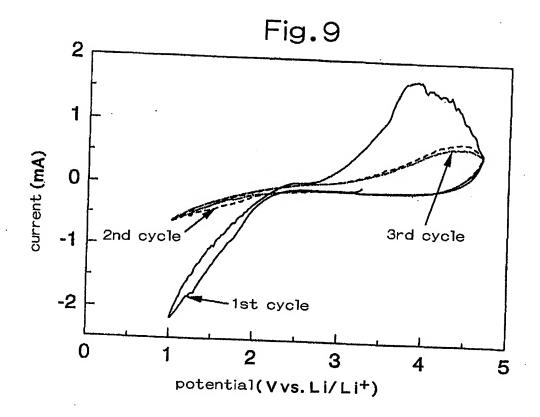


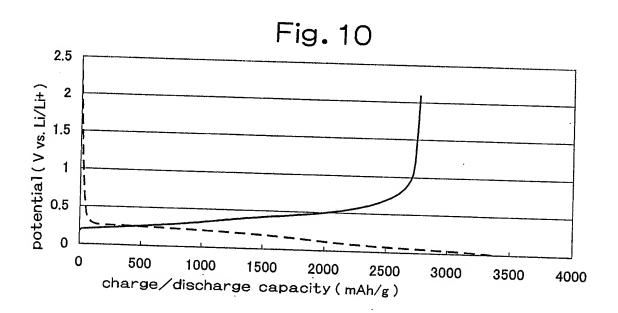


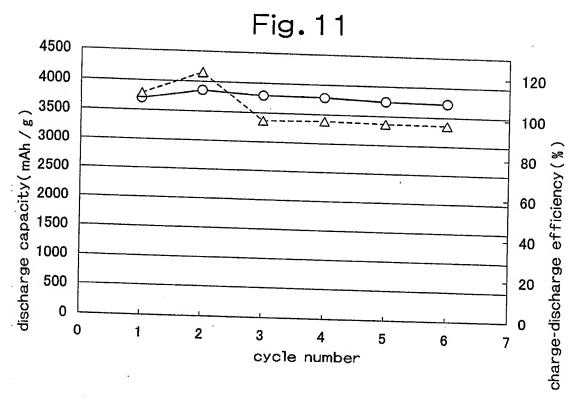


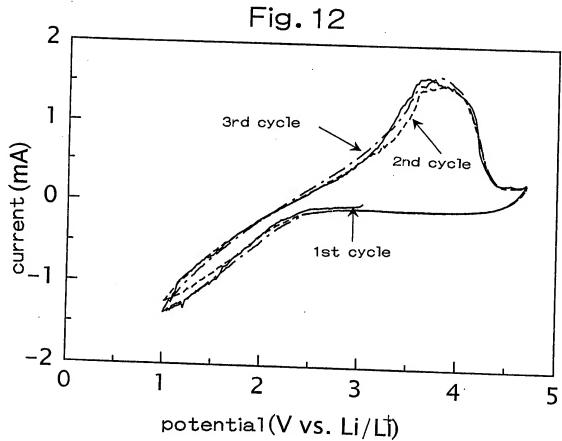


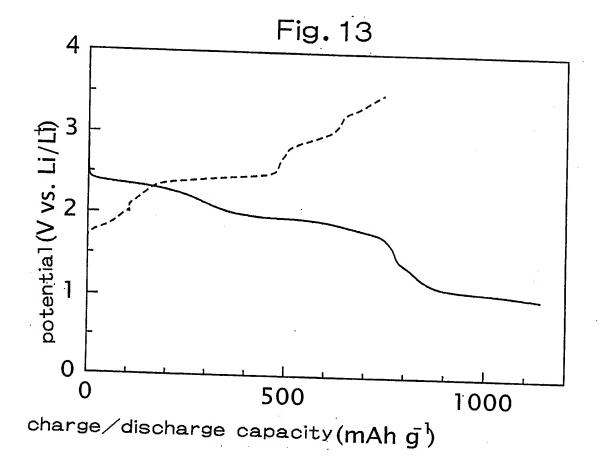


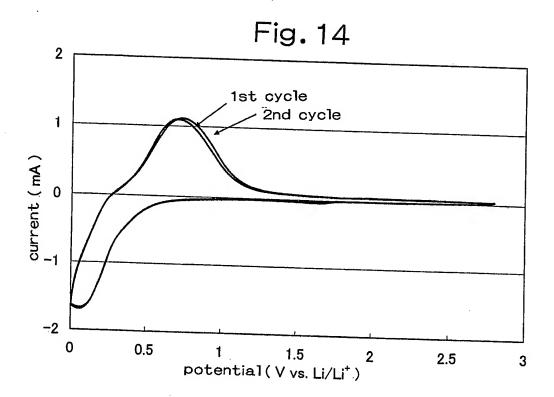


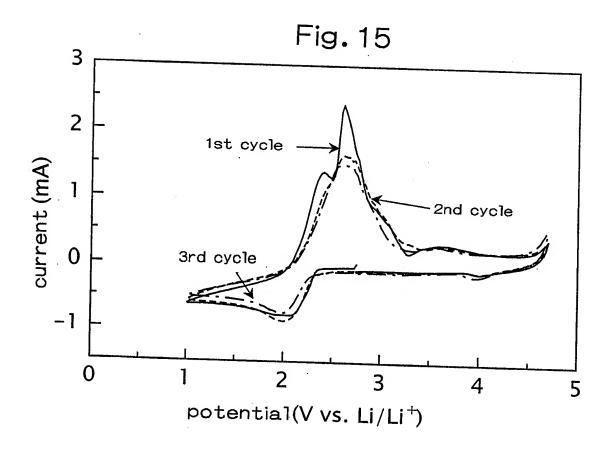


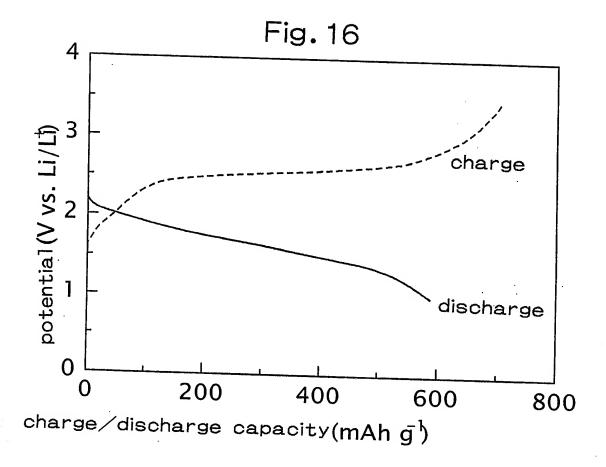


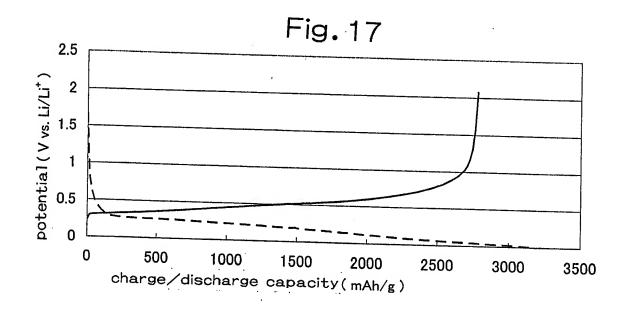


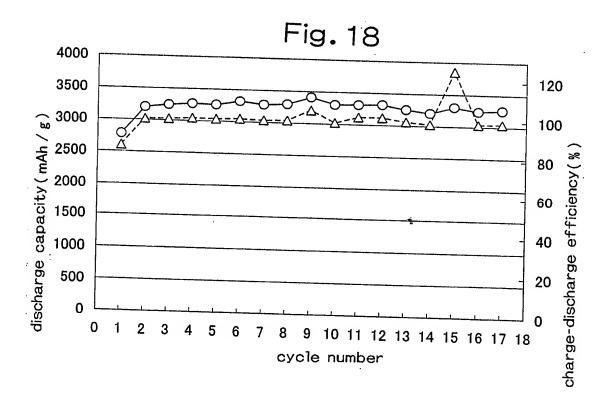


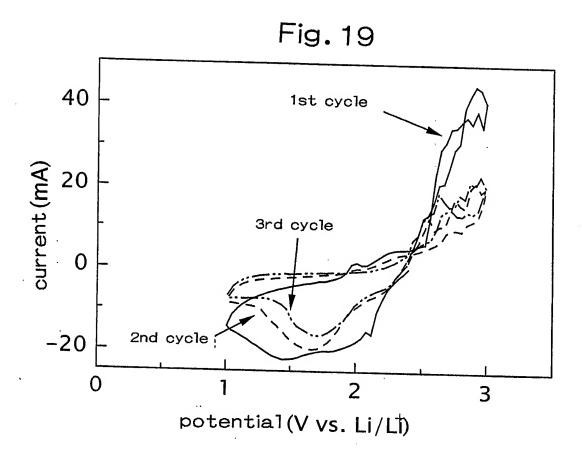


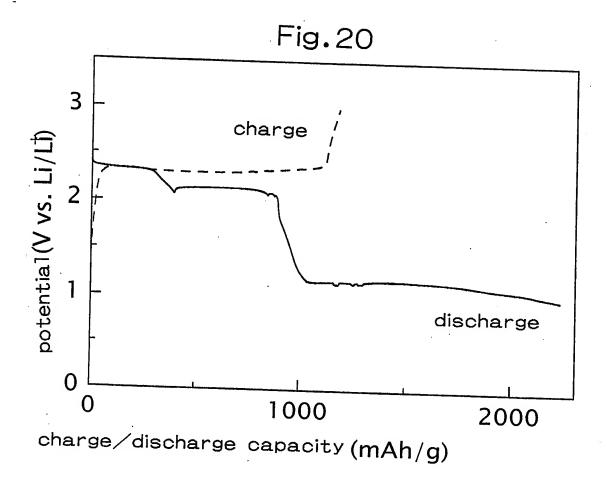


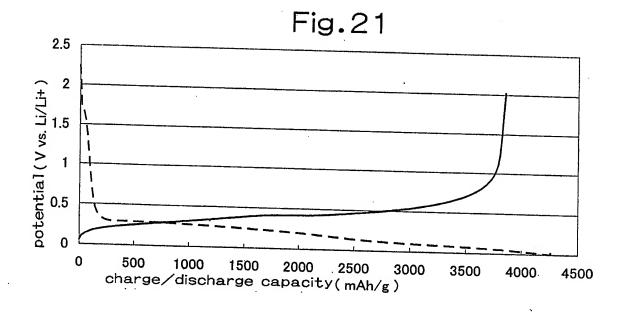


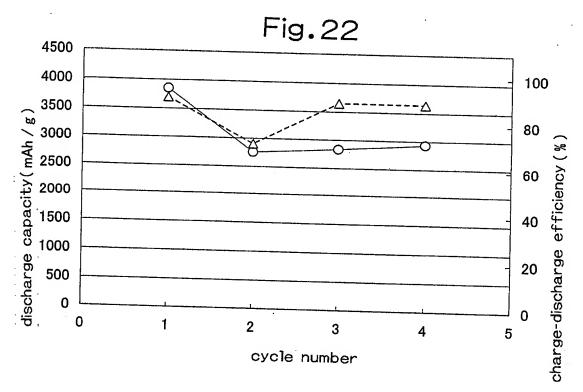


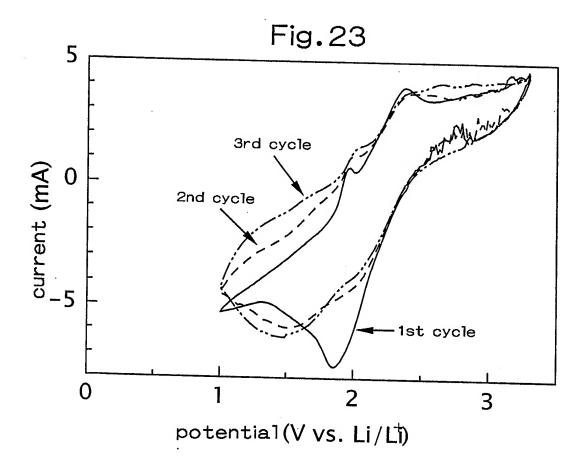


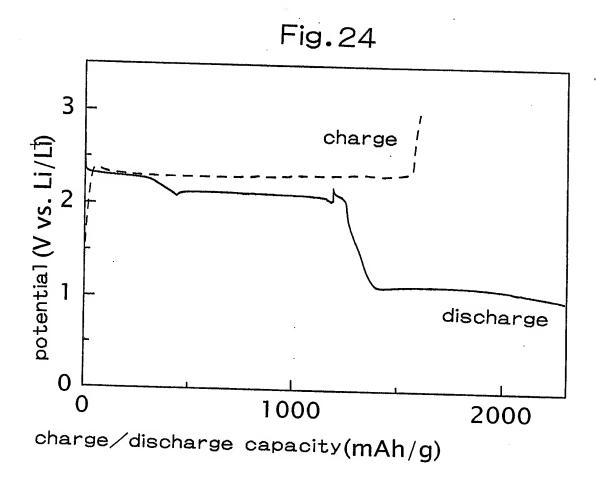


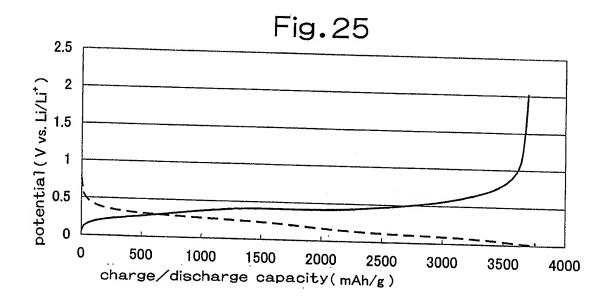


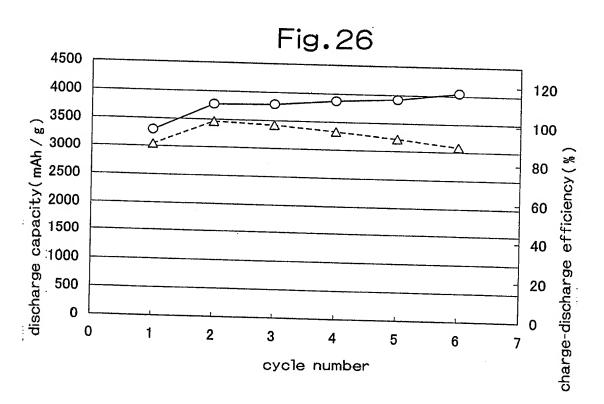


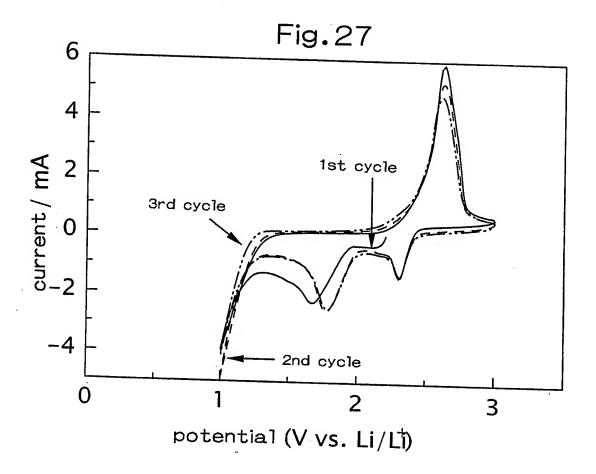


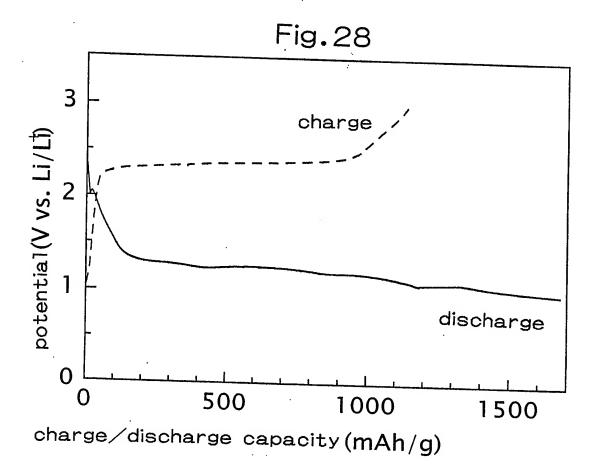


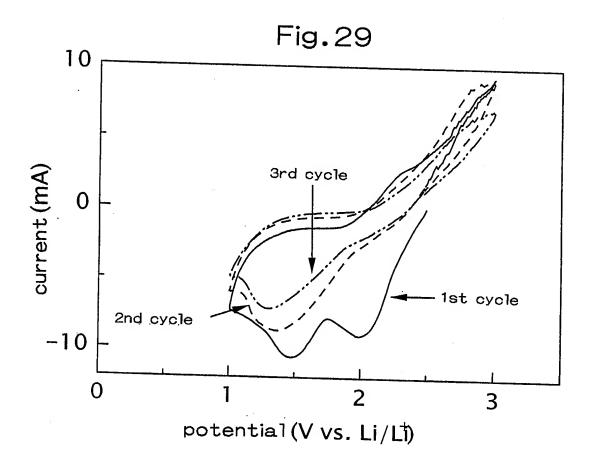


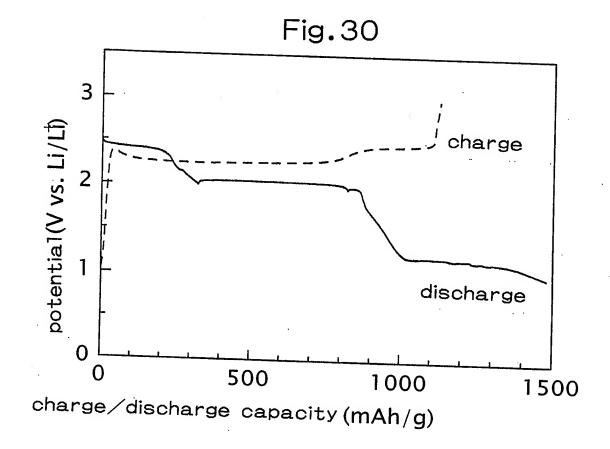


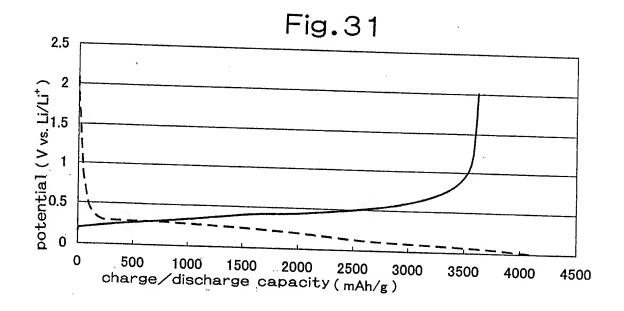


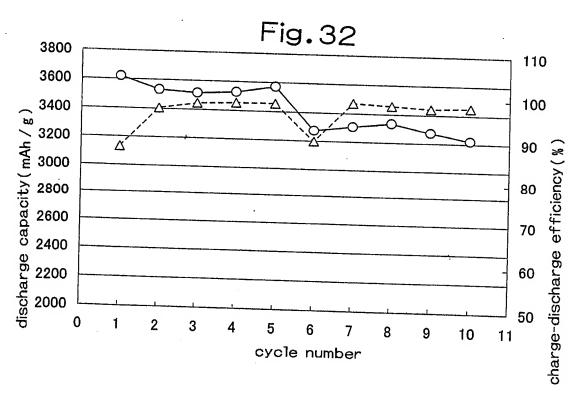


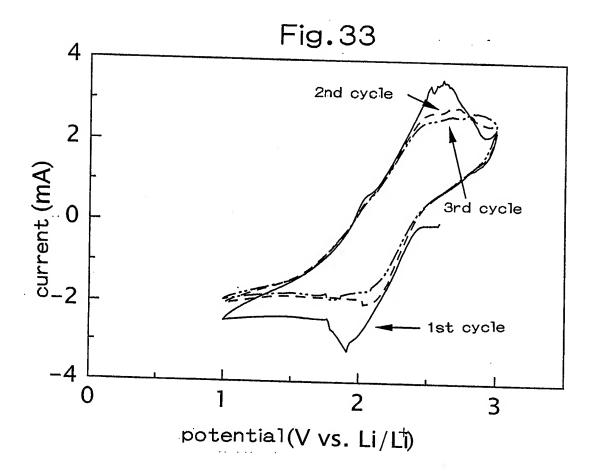


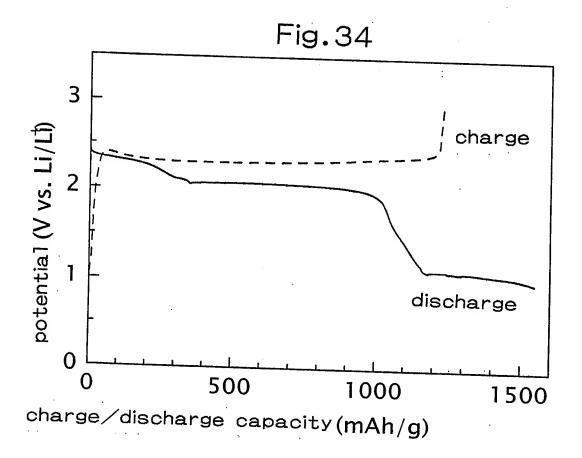


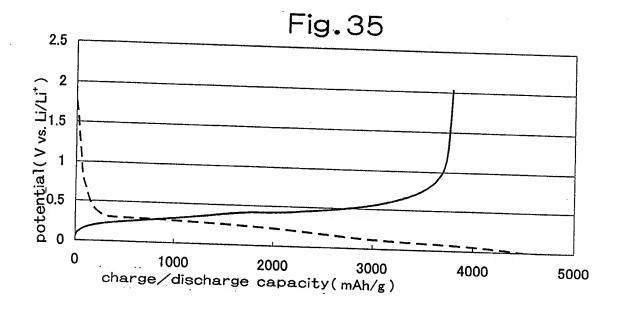


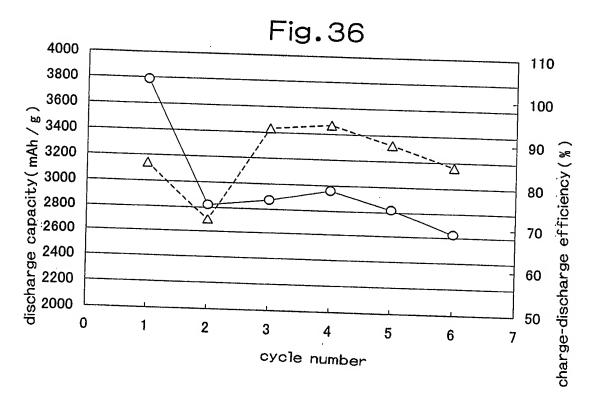


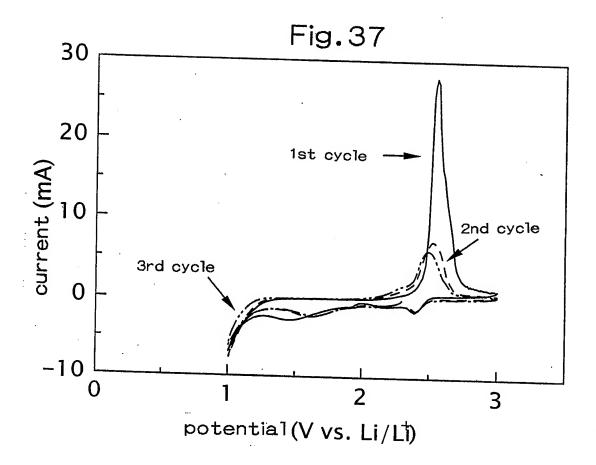


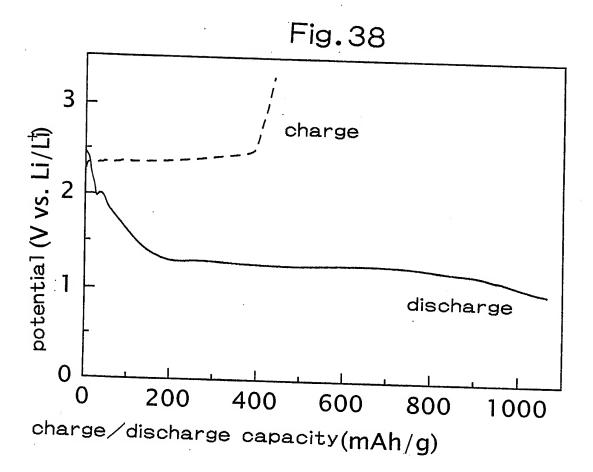


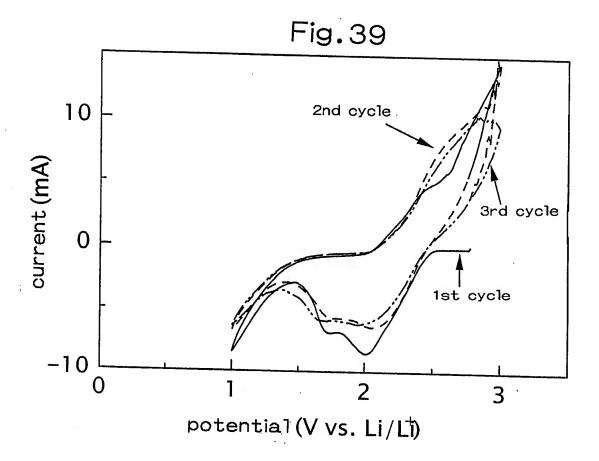


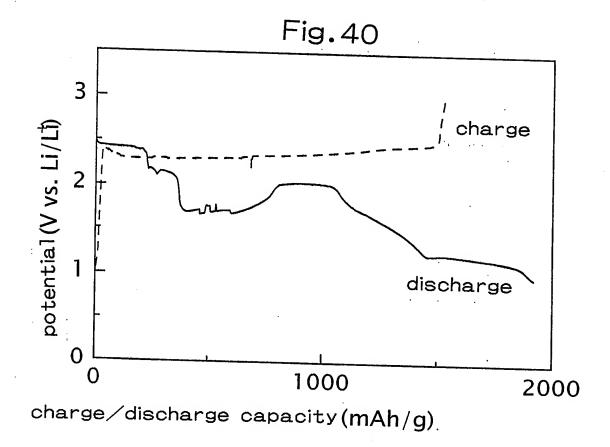


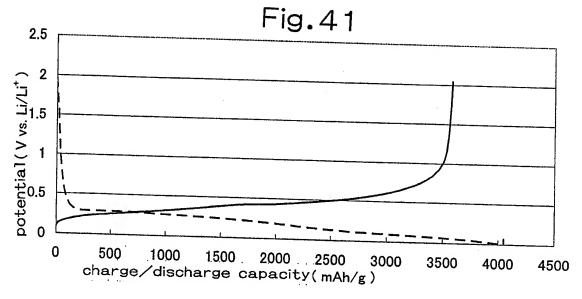


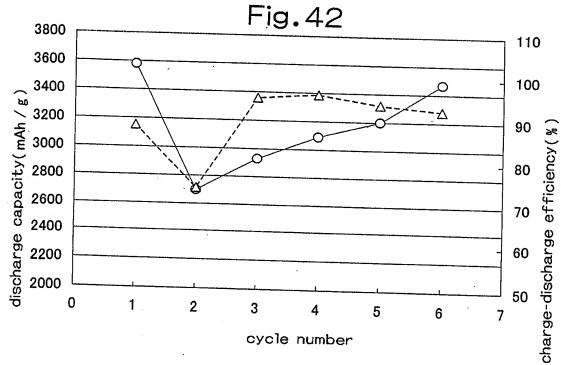


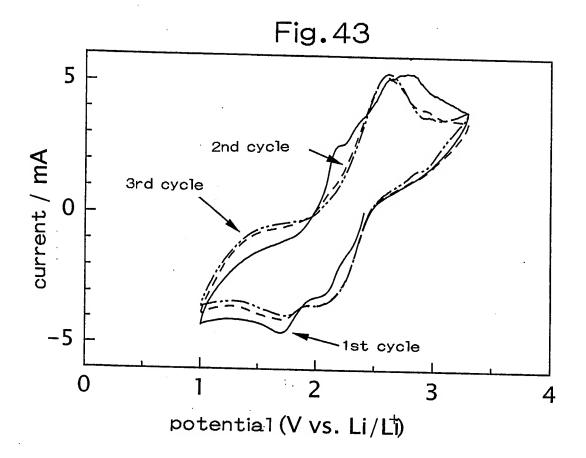


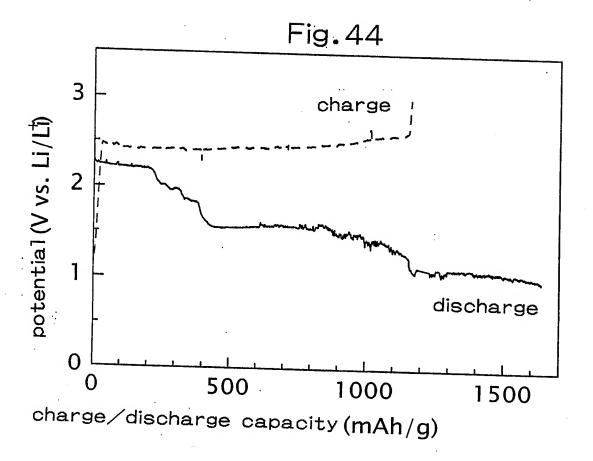


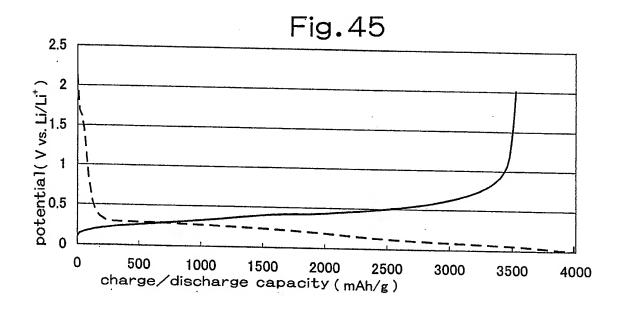


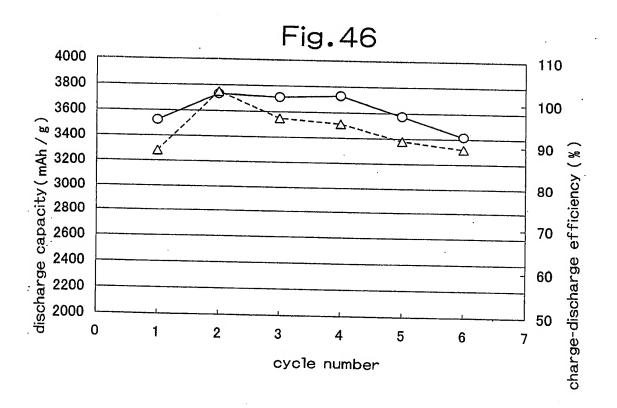


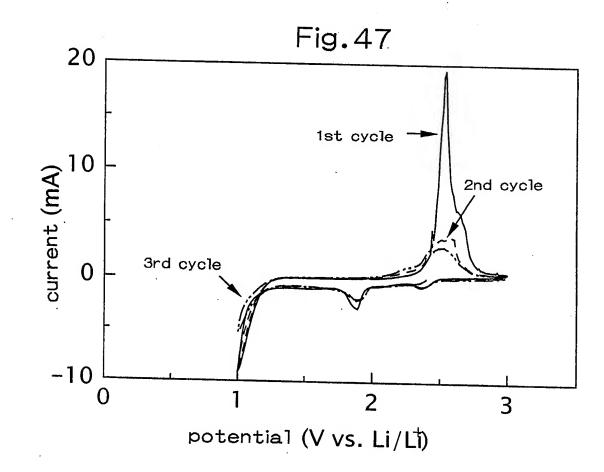


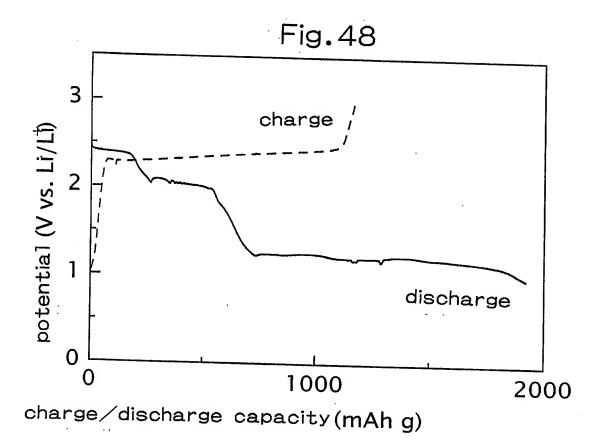












[Document Name] Abstract

[Abstract]

[Subject] A non-aqueous electrolyte secondary battery having increased capacity and energy density is provided.

[Solving Means] A non-aqueous electrolyte secondary battery comprises a positive electrode including elemental sulfur, a negative electrode including silicon that stores lithium, and a non-aqueous electrolyte including a room temperature molten salt having a melting point of not higher than 60°C.

10 The non-aqueous electrolyte may further include at least one type of solvent selected from cyclic ether, chain ether, and fluorinated carbonate. The non-aqueous electrolyte may include a room temperature molten salt having a melting point of not higher than 60°C and a reduction product of elemental sulfur.

[Selected Drawing] Fig. 1